Bis(dialkylamino)cyclopropeneimine Substituted Proton Sponge Derivatives: Synthesis, Theory, and Application

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Abstract

The work presented herein describes the synthesis, as well as the experimental and theoretical investigation of hitherto unknown cyclopropenimine containing compounds, mostly within the proton sponge backbone. The properties of these molecules are discussed in the context of other proton sponge derivatives reported in the literature. The superbasicity, catalytic activity, and fluorescent nature of these cyclopropenimine derivatives are also investigated and discussed.

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List of Abbreviations

AIM – Atoms in Molecules

AM1 – Austin Model 1

APA – Absolute proton affinity

BEMP – 2-tert-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine

BTMG – 2-*tert*-butyl-1,1,3,3-tetramethylguanidine

BTTP – P_1-t-Bu-tris(tetramethylene)

B3LYP –Becke's three parameter hybrid functional using Lee, Yang, and Parr's correlation.

CAHB – Charge assisted hydrogen bond

DABCO – 1,4-diazabicyclo[2.2.2]octane

DAC – Dialkylcyclopropenimine

DACN – 1,8-Bis(bis(diisopropylamino)cyclopropeniminyl)naphthalene

DBN –1,5-Diazabicyclo(4.3.0)non-5-ene

DBU – 1,8-Diazabicycloundec-7-ene

DCM – Dichloromethane

DFT – Density Functional Theory

DMAN – Dimethylaminonaphthalene

DMEGN – 1,8-bis(dimethylethyleneguanidino)naphthalene

DMSO – Dimethylsulfoxide

EPR – Electron Paramagnetic Resonance

GB – Gas phase basicity

HOMO – Highest Occupied Molecular Orbital

HMO – Huckel's Molecular Orbital

HMPN – 1,8-Bis(hexamethyltriaminophosphazenyl)naphthalene

ICT – Internal Charge Transfer

IEFPCM – Integral equation formalism, polarized continuum model

IHB – Intramolecular hydrogen bond

IR – Infra red

KHMDS – Potassium bis(trimethylsilyl)amide

LCAO – Linear combination of atomic orbital

LED – Light emitting diode

LUMO – Lowest unoccupied molecular orbital

MeCN – Acetonitrile

MO – Molecular orbital

NBO – Natural bond orbital

NHC – *N*-heterocyclic carbene

NICS – Nucleus independent chemical shift

NMR – Nuclear magnetic resonance

PA – Proton affinity

PTC – Phase transfer catalyst

TBAI – Tetrabutyl ammonium iodide

TBD – 1,5,7-triazabicyclo[4.4.0]dec-5-ene

TFA – Trifluoroacetic acid

TLC – Thin layer chromatography

THF – Tetrahydrofuran

TMGF – 4,5-bis(tetramethylguanidino)fluorene

TMGN – bis(tetramethylguanidino)naphthalene

UV – Ultra violet

VT – Variable temperature

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Prelude

Philosophical thought is inherent to our human consciousness. Many have spent lifetimes struggling to define the major questions of our existence. The most profound questions have always been philosophical in nature. The very fact that I have come into existence with the conscious ability to ask "why does anything exist at all?" is in and of itself an enigma. With my innate human inability to comprehend the vastness of time and space it is likely that I will never know the answer to this question or those of its nature. However, there is still much about my existence that I am able to learn and discover. It is for this reason that chemistry is such an appealing discipline. At the interface of biology and physics, with strong mathematical underpinnings, chemistry allows one to study the building blocks of life. I have always been drawn to Philosophy. In fact, there is very little in which I do not find genuine interest. This can be a burden, resulting in an endless feeling of intellectual deficiency. But in the end, making and analyzing molecules that may have never existed until I created them gives me great pleasure. I will be forever grateful to have had the privilege of exploring the building blocks of this world through research in chemistry.

Chapter 1 - Introduction

The terms “acid” and “base” are most often associated with their Brønsted-Lowry or Lewis definitions. Brønsted-Lowry acids and bases (commonly abbreviated to Brønsted acids and Brønsted bases) refer to compounds that donate or accept protons, respectively, while Lewis acids and bases refer to compounds that accept or donate electron pairs, respectively. The simplicity of these definitions is quite remarkable, considering the complexity of the underlying concepts, which evolved over many years, beginning even before the pioneering work of Arrhenius. The term “acid” originates from the Greek word “oxein”, a general word given to substances that tasted sour.[1] Oxein was then converted to “acetum” in the Latin languages, and eventually to “acid” in English.[1] The definition of acetum was first associated with vinegar (acetic acid) but was expanded to include all compounds that tasted sour, dissolved metals, and changed the colour of litmus paper. Its antonym, “base”, came afterwards and was first used as a term for substances which counteracted the effects of acids, but also for substances that felt slippery and tasted sour. Initially, the word “alkaline” was used to describe basic substances, and is derived from the Arabic word “al-qily”, which means “to roast in a pan” or “the calcinated ashes of plants”, since leaching the ashes of plants with water provided substances with basic properties (*e.g.*, KOH and NaOH).[1] As with the case that the word for base came after the word for acid, the chemistry of bases has notoriously lagged behind that of acids. This is most readily apparent from the relative frequency of using the name pK_a scale, compared pK_b scale, but can be witnessed in other aspects of chemistry as well, such as the prevalence of acid catalysis over base catalysis. It is in this

light that the research presented herein was undertaken, to further study lesser known, primarily basic compounds, specifically bis(dialkylamino)cyclopropenimines.

1.1 - Organic Bases and the Development of Superbases

Bis(dialkylamino)cyclopropenimines fall within a class of compounds known as "superbases". The term "superbase" is the result of impressive advancements within the many disciplines of chemistry, which have led to the development of increasingly stronger acids and bases. The strongest acid to have its acidity experimentally verified is fluoroantimonic acid,[2] and the strongest base to be experimentally verified is Schwessinger's *t*-Bu-P4 phosphazine base.[3] This remarkable range of acids and bases has necessitated terms such as "superacid" and "superbase". It should come as no surprise that the term "superacid" was coined well before the corresponding term for bases. A superacid has a well-established definition as a substance in which the chemical potential of a proton is higher than in pure sulfuric acid.[4] The term superbase, however, is somewhat more ambiguous and has been defined differently by different chemists. In his 1993 review article on the subject, Paul Caubere defined superbases in the following way: "*In this review the term superbase does not mean a base is thermodynamically and/or kinetically stronger than another. Instead it means that a basic reagent is created by combining the characteristics of several different bases. A superbase may be more efficient than its component bases in the case of some reactions and less efficient in others.*"[5] However, today the term superbase is generally associated with its thermodynamic strength, and is defined as any base having an absolute proton affinity (APA) larger than 245.3 kcal/mol and a gas phase basicity (GB) over 239 kcal/mol.[6]

Regardless, superbases have enormous practical utility and are of great theoretical curiosity, and thus continue to be thoroughly studied. The subclass of superbases most relevant to this work is that of the neutral, organic superbases. As the name implies, neutral, organic superbases are superbases that do not rely on metals or ionic charges for their basic strength. Consequently, this subclass of superbases is associated with high solubility in organic solvents, which makes them particularly attractive for synthetic applications.

1.2 - Neutral Organic Bases

The advent of neutral organic superbases came as a result of the development of neutral organic bases. One of the earliest reported syntheses of a neutral organic base was in 1957 when McKay and Kreling, at the Quebec-based Monsanto research laboratory, synthesized a series of bicyclic guanidines, including 1,5,7-triazabicyclo[4.4.0]dec-5-ene, commonly known as TBD (**1**, Figure 1).[7]

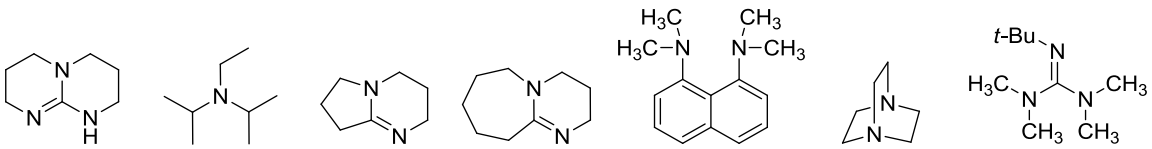


Figure 1. Selected nitrogen-based, neutral, organic bases.

As with all guanidines, the strong basicity of **1** comes predominantly from resonance stabilization of the positive charge associated with the conjugate acid, though the basicity of guanidines has also been attributed to Y-aromaticity,[8,9] charge stabilization through

intramolecular hydrogen bonding, and solvent stabilization.[10,11] The year following this synthesis, Hünig prepared *N*,*N*-diisopropylethylamine (Hunig's base, **2**)[12] as an improvement on the commonly used auxiliary base, trimethylamine. He postulated that increasing the steric bulk surrounding the amine nitrogen would afford a less nucleophilic base than trimethylamine, which would in turn prevent unwanted side reactions. Indeed, for this reason Hunig's base has become a staple reagent in organic synthesis. At the time, the impending utility of these newly reported organic bases in synthesis led to the preparation of other non-nucleophilic organic bases, such as the amidine bases, DBN (**3**) and DBU[13] (**4**). Not long afterwards, in 1968, Alder synthesized 1,8-dimethylaminonaphthalene (DMAN, **5**), which was found to be both exceptionally basic and non-nucleophilic, though it suffered from a low kinetic activity. Nevertheless, this work turned out to have a remarkable impact on our understanding of basicity (DMAN is discussed in great detail in ***Section 1.3***). In 1972, Ho, at the University of Manitoba, reported the use of 1,4-diazabicyclo[2.2.2]octane (DABCO, **6**) as a reagent for the dealkylation of quaternary ammonium compounds via transalkylation with other quaternary ammonium salts.[14] DABCO has since become a highly utilized organic base in many synthetic transformations. Then, in 1982 Barton synthesized a series of alkyl guanidines,[15] among which was 2-*tert*-butyl-1,1,3,3-tetramethylguanidine (BTMG, **7**), now commonly known as Barton's base. Though **7** had previously been made a decade earlier,[16] it was not properly characterized or used as a base in any chemical reaction. Barton discovered that not only was guanidine **7** a very strong base, but it had a very slow rate of methylation, and an even slower rate of benzylation. These properties, along with

the ease and low cost of its synthesis, made BTMG in many ways a superior base to DBN, DBU, DMAN, and Hunig's base.[17]

In 1987 Schwessinger introduced polyaminophosphazene bases (or simply, phosphazene bases) as a new class of neutral organic bases having the general structure $(R_2N)_3P{=}N{-}R$ (**8**, Figure 2).[18]

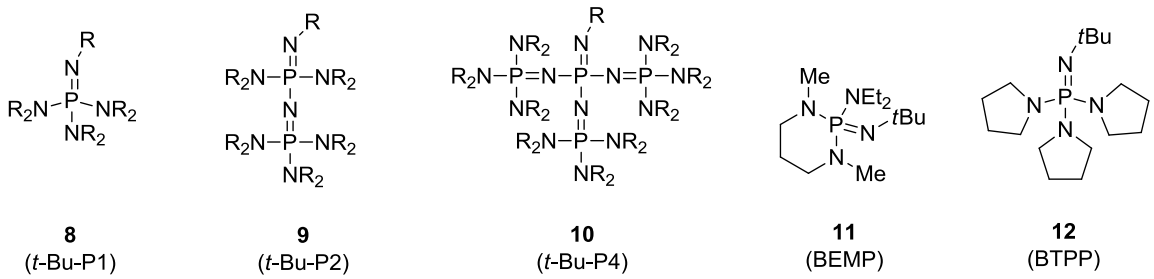


Figure 2. Selected polyaminophosphazene bases.

Schwessinger's approach of appending amino substituents to a central, basic phosphorus atom proved to have an extraordinary effect on its basicity, displaying pK_a values in MeCN up to 42.6. Schwessinger soon extended the original P1 system (**8**) by homologation of their chains (ex. *t*-Bu-P2, **9**, and *t*-Bu-P4, **10**). This was a marked improvement on the strength of organic bases, exemplified by Schwessinger's comments: "*We suspect that the phosphazene bases described here may define the limits of the strength of stable, uncharged nitrogen bases and may approach the limits of steric bulk within this extreme range of basicities*".[19] Nevertheless, structural improvements to Schwessinger's phosphazene bases still led to useful, albeit less basic, analogues such as BEMP and BTTP.[20] An example of their utility relevant to some of the work that will be

presented herein, is their involvement in the catalytic, enantioselective synthesis of α-amino acid derivatives as alternatives to phase transfer catalysis.[21]

Likely inspired by Schwessinger's work on phosphazenes, in 1989 Verkade improved upon his earlier design of highly unstable phosphatrane bases (example, **13**, Figure 3)[22] by employing amino-phosphorus linkages rather than alkoxy-phosphorus linkages (as seen in **15**, Figure 3).[23] The result was a highly stable phosphatrane base (**15**) that was 10^7 times more basic than any previously reported phosphine derivative. The stability of these caged phosphine bases comes, in part, from *trans*-annular N—P bond upon protonation (**14** and **16**, Figure 3).

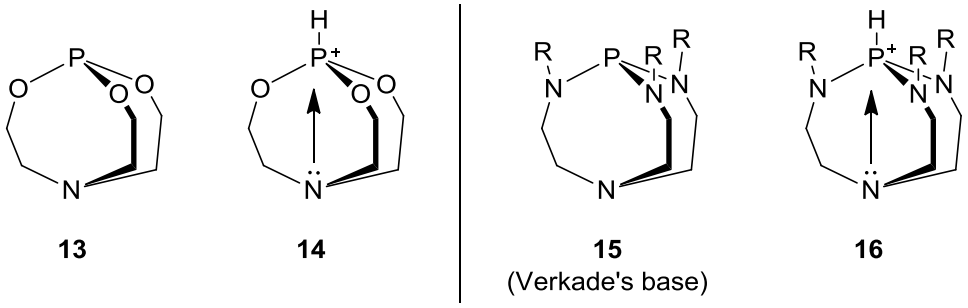
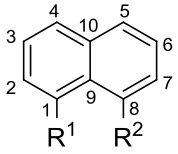


Figure 3. General structure of Verkade's phosphatrane base.

An interesting aspect of this work was the counter-intuitive finding that the primary amine linkers were more basic than secondary amine linkers. Nevertheless, it was found that **16** was not deprotonated upon refluxing with DBU in DMSO, *n*-BuLi in THF, CaH_2 in CH_2C1_2, or KOH in toluene. In fact, **15** was only regenerated upon slowly heating **16** to above **200** °C in anhydrous NaOH (no reaction was observed below 200 °C).

1.3 - Proton Sponges

In 1968 Roger Alder was studying the interaction between non-bonding electrons (*i.e.*, lone pairs) in 1,8-diaminonaphthalene (**17**, Figure 4) and discovered several principles of fundamental importance to our understanding of molecular interactions. Alder proceeded to successively methylate the amine substituents of **17**, and measure the resultant change in pK_a.[24] He found a modest increase in basicity after each successive methylation, until adding the fourth methyl group, when an unexpectedly large increase in pK_a was observed.



	R^1	R^2	pK_a
17	NH_2	NH_2	4.61
18	NHMe	NHMe	5.61
19	NHMe	NMe_2	6.43
5	NMe_2	NMe_2	12.34
20	$NMeCH_2Ph$	$NMeCH_2Ph$	

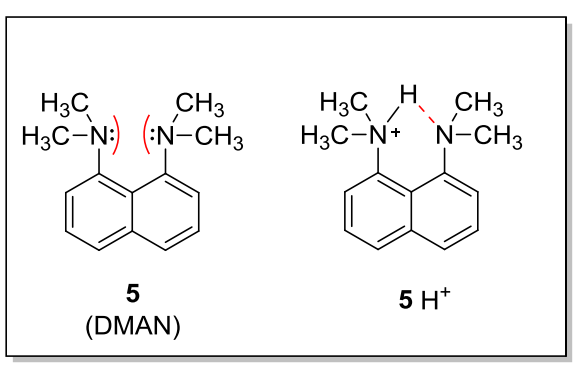


Figure 4. *N*-methylated derivatives of 1,8-diaminonaphthalene.

This strikingly large increase in pK_a upon introduction of the fourth *N*-methyl substituent was rationalized by Alder in the context of steric inhibition of resonance between the amine and the naphthalene backbone, van der Waals repulsion between the *N*-methyl groups, and dipole-dipole repulsions between the *N*-lone pairs. More specifically, the steric repulsion between the *N*-methyl groups forces the *N*-lone pairs to face inwards, towards each other. The resulting dipole-dipole repulsion between the two *N*-lone pairs destabilizes the molecule. Alder hypothesized that this strain could be partially alleviated

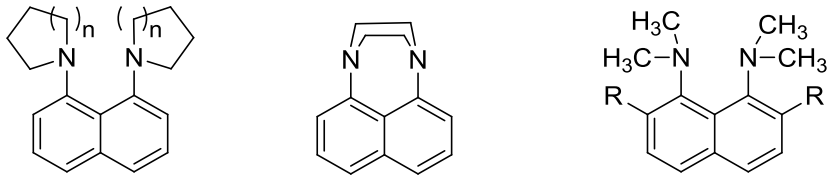
if the lone pairs were twisted out-of plane by 30 – 40° with respect to the aromatic ring. This angle would relieve some of unfavourable lone-pair repulsion, while maintaining sufficient *n*-π orbital overlap for partial electron delocalization into the naphthalene backbone. Evidence to this effect came from the change in chemical shift of the *ortho*-protons, indicative of a significant decrease in lone pair donation into the aromatic backbone, and the difference in the UV spectrum of **5** compared to **17**, **18**, or **19**. He further postulated that protonation (**5** H^+) would afford an NH—N intramolecular hydrogen bond (IHB), which would relieve the unfavourable lone pair-lone pair repulsion. This is well in line with the observed pK_a value, and further evidenced by the extremely deshielded signal for the N-H proton as well as the disappearance of the N-H stretch in the IR spectrum, consistent with existing reports of strong hydrogen bonding interactions.

Alder also noted the failure of **5** to alkylate in the presence of ethyl iodide after refluxing for four days in acetonitrile. This was particularly notable as existing organic bases suffered from unwanted *N*-alkylation, leading to undesired by-products. Though the exact spatial positioning of the methyl groups was unknown at the time, the poor nucleophilicity of **5** was attributed to the steric congestion around the two amine nitrogen atoms, which could accommodate nothing larger than a proton. However, thanks to the work of Einspahr and colleagues, the crystal structure of **5** was solved shortly thereafter.[25] Their analysis of the molecular structure indicated that the molecule was indeed strained, though surprisingly less strained than expected. There was noticeable distortion of the naphthalene backbone from ideal planarity, and the amino nitrogens were located above and below the plane of the central C-C bond. However, a symmetric alignment of the

NMe_2 groups above and below the plane of the backbone maintained significant *n*-π orbital overlap with the aromatic backbone. This was confirmed by the contracted N—C bond distances, which suggested ~20% π-character, and by subsequent Hückel Molecular Orbital (HMO) calculations, which supported these results. The N—N interatomic distance was found to be 2.79 Å, in contrast to that observed in the un-strained 1,8-bis(deutero)naphthalene, which has an D—D interatomic distance of 2.44 Å, or 1,8-diaminonaphthalene, which has an N—N interatomic distance of 2.45 Å. Based on an existing equation for non-bonding interactions,[26] the origin of the distortion from planarity (*i.e.*, the freebase strain) was not primarily a consequence of lone pair-lone pair repulsion, but rather steric repulsion between the methyl groups, as well as stabilizing CH—N interactions between the methyl hydrogens and the nitrogen atom. To accommodate the distortion from planarity, regardless of the origin, there was a noticeable elongation of the C(9)-C(8) and C(9)-C(1) bond distances in the backbone, and a contraction of the C(10)-C(4) and C(10)-C(5) bond distances.

The stereoelectronic considerations of 1,8-bis(dimethylamino)naphthalene, **5**, commonly known as Alder's "Proton Sponge"[i] sparked significant interest from other researchers over the next several decades. Accordingly, Alder expanded upon this concept by attempting to control the orientation of the *N*-lone pairs through various structural modifications (**21**, **22**, and **23**, Figure 5). [27]

[i] As far as I can tell from the literature, the term *Proton Sponge* was actually coined by Einspahr et al.[25] prior to being used as the trademark name by Aldrich.



21
a: n=1
b: n=2

22

23
a: R=OMe
b: R=Me

Figure 5. Selected examples of structurally modified proton sponges.

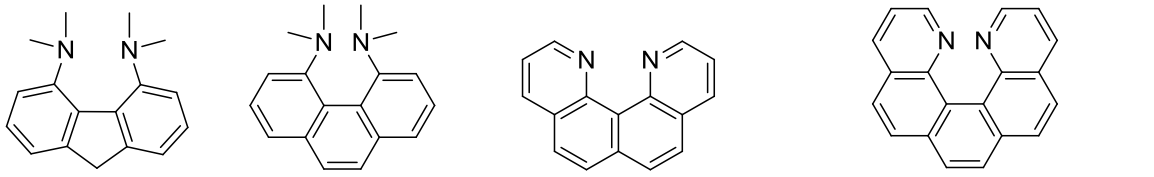
For example, he discovered that using ring systems, as in **21**, there is increased steric hindrance between the *N*-substituents and decreased communication between the *N*-lone pairs and the naphthalene backbone, leading to increased strain in the freebase and thus higher pK_a values. Additionally, while attempting to synthesize the bis-aziridine derivative of **21**, Alder inadvertently made compound **22**. He observed that by tethering the two nitrogen atoms together in this manner, all conjugation between the *N*-lone pairs and the naphthalene backbone was lost. This was determined from the carbon and proton NMR spectra, by the downfield chemical shift of the *ortho*- and *para*-carbon and hydrogen atoms, relative to those of other proton sponge derivatives.

Alder also found that substituents on the 2- and 7-positions of the naphthalene ring system (**23**a and **23**b) effectively reduced the N—N interatomic distance. The rationale is that these substituents ‘push’ against the *N*-alkyl groups, thereby forcing the alkylamino groups into closer contact. This is known as the "buttressing effect", and further increases the basicity of the resulting sponge by destabilizing the freebase and increasing the strength of the resulting hydrogen bond obtained upon protonation. In fact, when 1,8-bis(diethylamino)-2,7-dimethoxynaphthalamine (**22**a) was first synthesized in 1978[28] it was the strongest neutral organic base ever made, having a measured pK_a

between 16 and 17. Unfortunately, its high thermodynamic basicity and extremely low nucleophilicity was offset by a very low kinetic activity, which made it an impractical base for use in organic synthesis.

A notable property of these proton sponges is their inability to doubly protonate, even in the presence of strong acids. To this end, the pK_a of the protonated 1,8-bis(dimethylamino)naphthalene has been measured to be at least 20 pK_a units less than the freebase.[29] This was believed to be a consequence of the strong intramolecular hydrogen bond formed after the first protonation, in conjunction with the steric congestion around the amine lone pairs. Though the IHB present in proton sponges is thought to be somewhat unusual, given their short distance and inherent strength, the proton sponge proved tremendously useful to the ongoing exploration of hydrogen bonding. Prior to the development of proton sponges, the study of hydrogen bonding was restricted to intermolecular hydrogen bonding observed between molecules in the lattice of an x-ray structure. Proton sponges allowed chemists to directly probe the factors that affect the strength of a hydrogen bond using fixed interatomic distances. In 1972 Haselbach et al. used X-ray photoelectron spectroscopy to analyze the nature of the IHB in the proton sponge.[30] The evidence suggested a strong but unsymmetrical N-H—N hydrogen bridge. In their 1988 review, Staab et al. analyzed the geometry and basicity of existing proton sponge derivatives, and concluded that the hydrophobic shielding of the hydrogen bridge did not alter the pK_a, as previously thought.[31] Instead, they found this to be the underlying cause of their low kinetic activity, while the basicity is governed predominantly by the N—N interatomic distance and symmetry of the IHB.

In 1983 the term “proton sponge” was introduced by Aldrich Chemicals Co., Milwaukee, as a trade name for DMAN. Alder’s proton sponge had received considerable interest from the synthetic community as a highly basic, yet non-nucleophilic, neutral organic base. In this light, new proton sponge skeletons began to surface that same year in efforts to increase the basicity and/or the kinetic activity.[32] After analysis of the available data on proton sponges, Staab recognized that 1,8-diaminonaphthalene was perhaps not the ideal candidate for a "proton sponge", and implementation of the fluorene skeleton (*ex.* **24**, Figure 6) would be better suited for the role. Two important factors contributed to Staab’s choice of the fluorene backbone: the N—N interatomic distance is significantly smaller than in DMAN and the geometric orientation would provide a near linear alignment of the *N*-lone pairs along the N—N plane. This would not only increase ground state destabilization, but would result in a linear hydrogen bond, which is generally accepted to be stronger.



24 (Fluorene) **25** (Phenanthrene) **26** (Quino[7,8-h]quinoline) **27** (Benzo[1,2-h:4,3-h’]diquinoline)

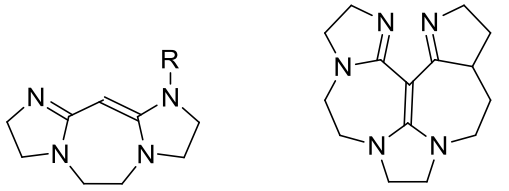
Figure 6. Selected examples of proton sponge derivatives with backbones other than 1,8-diaminonaphthalene.

The synthesis of bis(dimethylamino)fluorene (**24**) was accomplished by methylation of diaminofluorene with dimethylsulfate and sodium hydride, achieving a 90% yield. As expected, **24** was isolated as the monoprotonated salt, and was not susceptible to di-protonation, even in the presence of strong acids. Furthermore, the X-ray structure

indicated a nearly linear N-H—N hydrogen bridge. When **24** was added to DMAN•$HClO_4$ in a 1:1 mole ratio, the ^{1}H-NMR spectrum showed almost complete deprotonation of DMAN, and conversion of **24** to its protonated salt. Additional UV/vis spectroscopic analysis measured the pK_a of **24** to be 12.8, 0.5 pK_a units above that of DMAN.[33] Additional modification saw successful implementation of the phenanthrene backbone (**25**, Figure 6) to increase basicity. It was expected that a decreased N—N interatomic distance would increase the freebase strain as well as the strength of the corresponding hydrogen bond. A subsequent X-ray crystal structure confirmed the decreased interatomic distance and a short, linear hydrogen bond, though it was found to be less basic than DMAN, having a pK_a of 11.5. The origin of this lower basicity was believed to be due to the fact that the hydrogen bond was less shielded by the surrounding methyl groups, which decreases its thermodynamic stability. Then in 1987 Staab expanded the definition of proton sponges beyond "*bis(dialkylamino)arenes whose dialkylamino groups are in close spatial proximity*",[34] by introducing the quino[7,8-h]quinolone backbone (**26**, Figure 6). Though several syntheses of this molecule had already been reported, the structural assignments were later discovered to be incorrect, and thus Staab's synthesis represents the first. This was confirmed shortly thereafter with X-ray crystallographic analysis.[35] Notably, this new type of proton sponge lacked the hydrophobic shielding associated with the *N*-alkyl substituents, which has the beneficial effect of increasing the kinetic activity of **26** while maintaining a high thermodynamic basicity (pK_a = 12.8). Staab then synthesized the next higher benzologue, benzo[1,2-h:4,3-h']diquinoline (**27**, Figure 6) and obtained its X-ray crystal structure.[36] **27** was found to be a significantly weaker base than **26**, having a pK_a of only 10.3. The origin of

its lower thermodynamic basicity was attributed to its helical geometry, which allows the basic pyridinium nitrogen atoms to reside in different spatial planes and avoid lone pair-lone pair repulsion and the accompanying freebase strain.

Meanwhile in 1987, in addition to his work on polyaminophosphazenes, Schwessinger introduced the vinamidine unit (**28**, Figure 7)[37] in conjunction with the vinamidine proton sponge (**29**, Figure 7).[38]



28
(vinamidine)

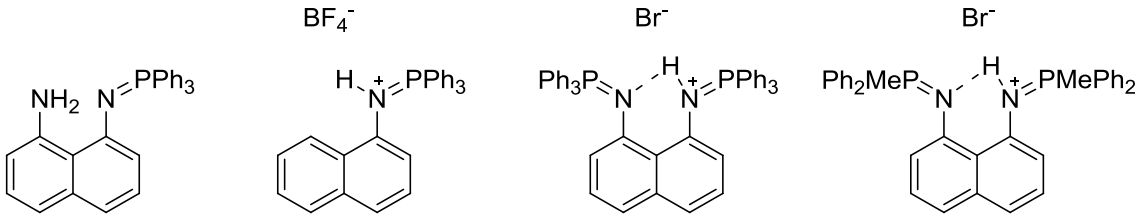
28a R = H
28b R = CH_3

29
(vinamidine
Proton Sponge)

Figure 7. Schwessinger's vinamidine base and vinamidine proton sponge.

The vinamidine unit was proposed to be a strong base, owing to the planarity of its protonated salt, which would allow for optimal resonance stabilization of the positive charge. This theory was validated when the pK_as of **28a** and **28b** in acetonitrile were measured at 26.22 and 26.95, respectively, making **28** a more basic unit than DBU. Not surprisingly, it was then found that the proton sponge variant of the vinamidine unit (**29**) was more basic than vinamidine itself, having a pK_a three units higher (29.22). Furthermore, in agreement with Staab's work, the lack of hydrophobic shielding in **29** resulted in a high kinetic activity, though it was also found to be substantially more nucleophilic and prone to alkylation. Moreover, **29** could be obtained as its di-protonated salt in the presence of excess acid.

Though modifications to the proton sponge backbone, through electronic effects, buttressing effects, and alternate molecular frameworks, proved fruitful, modification of the *N*-substituents resulted in far more dramatic increases to the pK_a of proton sponges. Though such modification began early after Alder's seminal publication,[24] the first true advancement in this regard came in in 1991, when two Spanish research groups, who had been studying iminophosphoranes and their basicity, recognized the possibility of synthesizing an iminophosphorane-substituted proton sponge derivative.[39,40] In the first part of their two-part report, the authors added triphenylphosphonium bromide to 1,8-diaminonaphthalene to afford the corresponding 1-amino-8-triphenylphosphoranylideneaminonaphthalene (**30**, Figure 8). The authors also reported the first X-ray structure of the parent compound, 1,8-diaminonaphthalene (**17**), which was compared with that of **30**. The most notable features were an increased distortion from planarity of the naphthalene backbone in **30**, relative to **17**, as well as a shorter and more linear IHB.



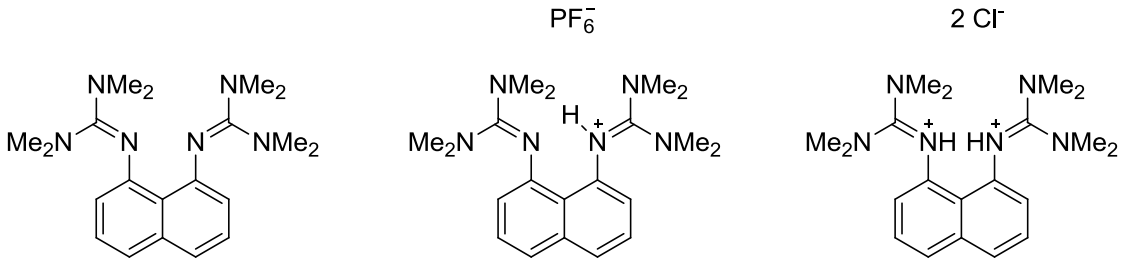
30 **31** **32** **33**

Figure 8. Iminophosphorane-proton sponge derivatives.

A rather fascinating aspect of this publication, from a historical standpoint, is that the authors used the semi-empirical AM1 method to compute the molecular geometry of **17** and not **30** because**:** "*It is at present practically impossible to carry out similar*

calculations on compound 2 (labelled compound **30** in this thesis)**,** *owing to both the number of atoms and the torsion angles.*"[39] In the second part of their report, the authors described the syntheses and crystal structures of **31**, **32**, and **33** (Figure 8). The replacement of a phenyl group (**32**) with methyl (**33**) did not result in any significant changes in the rigid backbone of the molecule. Consistent with existing crystallographic data on proton sponges, compounds **32** and **33** had their nitrogen atoms distorted out of the plane of the naphthalene ring, in opposite directions. In addition, the authors observed the presence of a short and linear IHB.

It is likely that this work sparked the beginning of a new trend in proton sponges, in which increasingly basic units are added as substituents to the nitrogen atoms. The next example came a decade later in 2002 with the synthesis of 1,8-bis(tetramethylguanidino)naphthalene (TMGN, **34**, Figure 9) by Sundermeyer et al., which incorporated guanidine substituents onto the naphthalene backbone.[41]



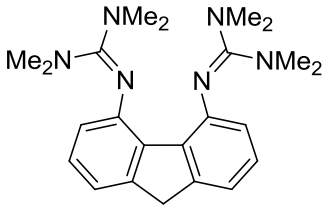
34 (TMGN) **35** **36**

Figure 9. The 1,8-bis(tetramethylguanidino)naphthalene proton sponge (TMGN, **34**) and its congeners.

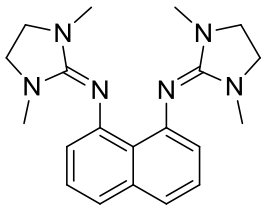
Notably, this report marked the first instance where the three factors that influence the basicity of proton sponges were clearly outlined. These three factors were described as: i)

destabilization of the base as a consequence of strong repulsion of unshared electron pairs, ii) formation of an intramolecular hydrogen bond (IHB) in the protonated form, and iii) relief from steric strain upon protonation. The authors decided to alter the *N*-substituents with peralkylguanidine units, which were among the strongest neutral organic bases known at the time. The synthesis involved the addition of two equivalents of the Vilsmeyer salt, tetramethylchloroformamidinium chloride, to one equivalent of 1,8-diaminonaphthalene in MeCN, with triethylamine as an auxiliary base. Similar to Schwessinger's vinimidine proton sponge, TMGN was found to be kinetically active and prone to bis-protonation in the presence of strong acids. However, only the monoprotonated salt was formed in the presence of excess NH_4PF_6. Accordingly, the authors were able to obtain crystal structures of the mono-protonated salt (**35**), the bis-protonated salt (**36**), and the freebase (**34**). The molecular structure of the **34** was found to possess significant freebase strain, as evidenced by the distortion of the naphthalene backbone from planarity and the positioning of the anilino nitrogen atoms above and below the ring. The sp^2 nature of these imine nitrogens facilitates the out-of-plane orientation, and allows for more freedom of the planar guanidine groups to avoid steric repulsion when they are on opposite sides. The monoprotonated salt, **35**, adopted the same C2-symmetrical orientation as **34** (though deviation from perfect C2-symmetry was observed), wherein the anilino *N*-atoms were positioned above and below the ring, placing the guanidine groups on opposite sides. However, the presence of a short, unsymmetrical IHB resulted in a decreased N-N interatomic distance and a noticeable decrease in distortion from planarity. The bis-protonated salt, **36**, changes geometry somewhat dramatically. Instead of an IHB, the two acidic protons are involved in a

bifurcated hydrogen bond to a chloride counterion. As a result, the two N-atoms are actually nearly in the plane of the naphthalene backbone, with the gauanidine units adopting a *syn*- rather than *anti*-orientation. UV/Vis spectroscopic titration was not possible, as the corresponding spectra of **34** and **35** were too similar. As such, the authors used ^{1}H-NMR transposition experiments in MeCN-d3 to measure the pK_{BH+} of **34** (or pK_a of the conjugate acid), which was found to be 25.1.



37
(TMGF)

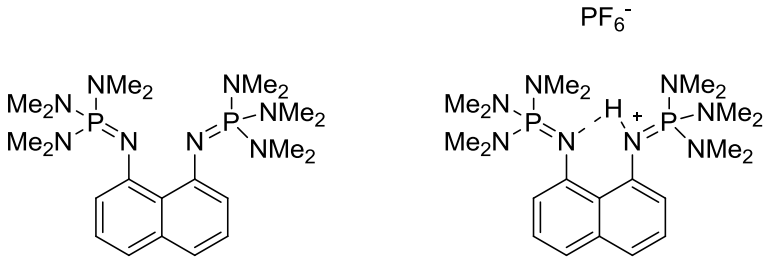


38
(DMEGN)

Figure 10. Guanidine substituted proton sponges, TMGF (**37**), and DMEGN (**38**).

Notably, the following year, Maksić and Kovačević used computational methods to explore the origins of its basicity.[42] Surprisingly, it was found that TMGN displayed almost no freebase strain, and its high basicity is a consequence of the inherent basicity of the guanidine unit and the ensuing IHB. They also compared TMGN with TMGF (**37**, Figure 10), a guanidine substituted proton sponge possessing a fluorene backbone instead of naphthalene. The authors found that in addition to a modest increase in its IHB strength, there was substantially more freebase strain within **37**, making it a much stronger base than TMGN. Furthermore, Sundermeyer at coworkers expanded on this work the following year with a cyclic guanidine derivative, 1,8-bis(dimethylethyleneguanidino)naphthalene (DMEGN, **38**), though it was found to be less basic than TMGN.[43]

The next notable derivative came when these two research teams collaborated on the synthesis and theoretical investigation of a bisphosphazine proton sponge, 1,8-bis(hexamethyltriaminophosphazenyl)naphthalene (HMPN, **39**, Figure 11) in 2005.[44] The synthesis involved the addition of two equivalents of [P(NMe$_2$)Br]Br to 1,8-diaminonaphthalene in chlorobenzene, with triethylamine as an auxiliary base. Protonation with ammonium hexafluorophosphate yielded the monoprotonated salt, **40**.



39 (HMPN) **40**

Figure 11. Phosphazine-substituted proton sponge HMPN (**39**) and its HPF_6 salt (**40**).

This combination of Alder's Proton Sponge and Schwessinger's basic phosphazine unit resulted in a kinetically active and highly basic molecule with a pK_a of 29.9. Unlike TMGN, HMPN was only isolated as its monoprotonated salt. X-ray diffraction analysis revealed that the freebase, **39**, was nearly C2 symmetric, but had distortion of the naphthalene backbone. Upon protonation, an IHB is formed, which relieves strain. The authors used homodesmodic reactions to calculate the effect of freebase strain and intramolecular hydrogen bond energy on the basicity of HMPN, finding that they contributed 14.9 and 9.5 kcal/mol, respectively.

All things considered, this interplay between molecular strain, intramolecular hydrogen-bond energy, and basicity which has been studied so thoroughly in proton

sponges, has led to many scientific insights that have undoubtedly influenced our fundamental understanding of chemistry, far beyond just the prototypical proton sponge. In particular, the study of hydrogen bonding (H-bonding) within proton sponges has provided rigorous knowledge into the interrelated roles of symmetry, resonance, and aromaticity in H-bonding, as well as a better understanding of kinetic vs. thermodynamic basicity and the emergence of a more refined view of the entropic and enthalpic factors contributing to H-bond strength.[45] Of biological relevance, the knowledge gained from proton sponges has provided further insight into amide *N*- vs *O*-protonation states and the mechanism of acid-catalyzed amide hydrolysis in peptides, in addition to fostering a more informed understanding of the importance of short and strong hydrogen bonding in various enzymatic processes.[46] Meanwhile, overshadowing these developments, at least from a fundamental stance, has been the influential impact they have had on current theories surrounding proton transfer rates,[47] charge transfer states,[48] and unusual hydrogen bonding.[49]

1.4 - Cyclopropenes and Related Compounds

Much like the proton sponge (**5**), the bis(dialkylamino)cyclopropenimine (DAC) motif began as nothing more than a theoretical curiosity,[50] a simple extension of the cyclopropyl cation.[51] However, continued study has led to numerous insights into their chemical and electronic properties,[52] and DACs have since found applications in organocatalysis[53] and phase transfer catalysis[54] or, alternatively, use as ionic liquids,[55] polyelectrolytes,[56] components of nitrogen based ligands,[57] and superbases.[58]

The cyclopropyl cation is the smallest possible carbon-based aromatic molecule and has thus been of longstanding interest to physical organic chemists. Its study began with the cyclopropene core, for which the first confirmed synthesis was reported in 1922 by Dem'yanov and Doyarenko through the thermal decomposition of trimethylcyclopropyl ammonium hydroxide.[59] The following year Goss, Ingold, and Thorpe reported two different synthetic approaches to methylcyclopropene dicarboxylic acid (**41**, Figure 12),[60] the structure of which was supported by evidence from the syntheses themselves and subsequent chemical transformations.

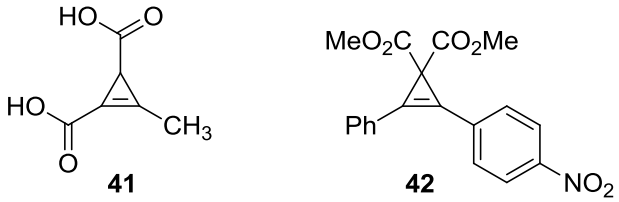


Figure 12. Early reported examples of cyclopropene derivatives (**41** and **42**).

However, Goss et al. incorrectly assumed that the methylene proton, which they termed the "*mobile hydrogen atom*", was essential for the stability of cyclopropenes. This notion was challenged by Kohler and Darling in 1930 while investigating cyclopropene derivatives as intermediates in the base mediated transformation of nitrocyclopropanes to unsaturated open chain compounds.[61] Kohler and Darling hypothesized that in the absence of a hydrogen atom and any electron withdrawing group, cyclopropene derivatives would be sufficiently stable in the presence of strong bases or nucleophiles. Their successful synthesis and identification of tetrasubstituted cyclopropene derivative **42** (Figure 12) proved that the stability of cyclopropenes was not restricted to derivatives having a "mobile hydrogen".

This preliminary work on the stability of cyclopropenes led to the ensuing interest in cyclopropyl cations. The first evidence that the cyclopropyl cation possessed enhanced stability through electron delocalization (*i.e.*, aromaticity) came in 1952.[62] Roberts et al. were applying Huckel's linear combination of atomic orbitals (LCAO) method to calculate the delocalization energy of an array of small organic molecules and found that the cyclopropene cation (**43**, Figure 13) possessed high delocalization energy, indicative of aromatic stability.

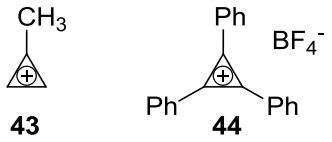
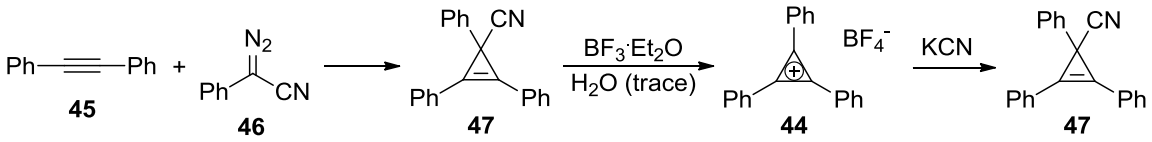


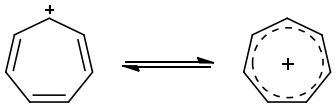
Figure 13. The cyclopropyl methyl cation (**43**) and the *s*-triphenylcyclopropenyl cation (**44**).

However, Huckel's LCAO method considers only the molecule's π–electrons and there was some speculation as to whether the ring strain of a three-membered σ–framework would supersede the stability of π-delocalization. This debate was settled in 1957 when Breslow reported the synthesis and isolation of the *s*-triphenylcyclopropenyl cation, **44** (Scheme 1).[63] The synthesis of **44** proceeded through a triphenylcyclopropenenitrile intermediate (**47)**, which was synthesized from the reaction between phenyldiazoacetonitrile (**45**) and diphenyl acetylene (**46**).

Scheme 1. Breslow's synthesis of the s-triphenylcyclopropenyl cation (**44**).



Reaction with boron trifluoride etherate and a trace amount of water (analogous to the known procedure for preparing the cycloheptatrienyl cation[64]) afforded **44** as a white crystalline solid. The identification of **44** was confirmed by elemental analysis, conversion to the picrate salt, and the regeneration of **47** upon addition of potassium cyanide. It was also around this time that von Doering and Knox characterized the next higher homologue of the cyclopropyl cation, the cycloheptatrienyl cation (**48**, Figure 14),[65] though its synthesis was first reported by Merling in 1891.[66]



48
(tropylium cation)

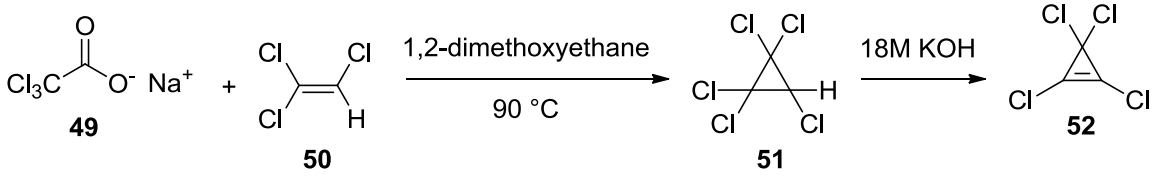
Figure 14. Structure of the cycloheptatrienyl cation (*i.e.*, the tropylium cation, **48**).

As for the cyclopropyl cation, the aromatic stabilization of the tropylium cation was predicted prior to its isolation. The prediction came from Huckel in 1931 during the development of quantum mechanics and the theory of aromaticity,[67] and was then corroborated by Roberts using the LCAO method in 1952.[51] The isolation of the tropylium cation was not only further confirmation of Huckel's theory, but its experimentally defined stability explained the reactivity of some related compounds, which likely proceeded through tropylium cation intermediates.

Shortly thereafter, in 1959, Wagner unknowingly made a vital contribution to the development of cyclopropenimines when he reported the thermal decarboxylation of sodium trichloroacetate as a new approach to the synthesis of dichlorocarbene.[68] Upon refluxing a 15% solution of sodium trichloroacetate (**49**) in 1,2-dimethoxyethane, he obtained sodium chloride in nearly quantitative yield. It was postulated that without the

presence of a proton donor, the intermediate CCl_3^- Na^+ would dissociate into the $:CCl_2$ carbene and NaCl. The presence of $:CCl_2$ was confirmed by *in situ* reaction with alkenes, which were known carbene acceptors. Reaction with cyclohexene and cycloheptatriene provided 7,7-dichloronorcarane and 8,8-dichlorobicyclo[5,1,0]octa-2,4-diene in 47% and 46.5% yield, respectively. A few years later in 1963, Tobey and West used this methodology to synthesize pentachlorocyclopropane (**51**, Scheme 2).[69] By refluxing sodium trichloroacetate in 1,2-dimethoxyethane in the presence of trichloroethylene, they were able to obtain pentachlorocyclopropane, **51**, in 25% yield. The authors made particular note of the troublesome purification, as it was discovered that thermal decomposition occurred below the product's boiling point, and vacuum distillation below temperatures of 100 °C was required.

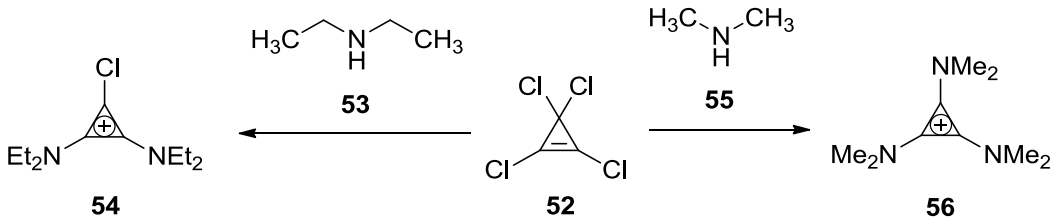
Scheme 2. Tobey and West's synthesis of pentachlorocyclopropane (51) and trichlorocyclopropene (**52**).



The authors then discovered that simply shaking **51** in an 18 M solution of KOH, induced E2 elimination to provide tetrachlorocyclopropene, **52**, in 85% yield. Confirmation of the structure was provided by IR and Raman spectroscopy. Additionally, chlorination of tetrachlorocyclopropene under UV light provided hexachlorocyclopropane, which had been made using a different route the same year. Continued research led Tobey and West to the synthesis of the trichlorocyclopropenium ion in 1964 by reacting tetrachlorocyclopropene with $AlCl_3$,[70] which represents one of the simplest possible

aromatic systems, having only six atoms, consisting of only two different elements. This work was followed shortly thereafter by Breslow, who established the pK_R of several cyclopropyl cations, including triphenyl, isopropyl diphenyl, and triisopropyl cyclopropyl cation.[71] The results suggested that alkyl groups provide more stabilization to the cyclopropyl cation than phenyl groups. With this in mind, in 1971 Yoshida placed alkylamino substituents on the cyclopropene core to yield the first aminocyclopropenium ion (**56**, Scheme 3).[72] By simply reacting tetrachlorocyclopropene with excess secondary amine, followed by the addition of excess perchloric acid, Yoshida was able to obtain the corresponding triaminocyclopropenyl cations in quantitative yields and excellent purity.

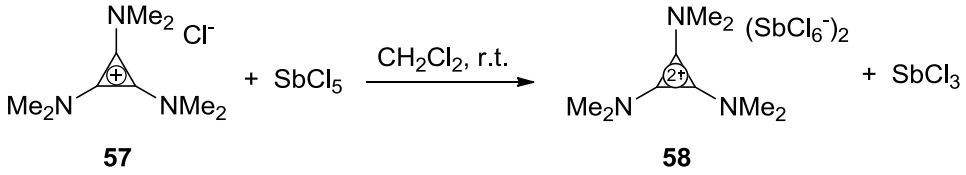
Scheme 3. Yoshida's method for the synthesis of aminocyclopropenyl cations.



An exception was the reaction with diethylamine (**53**), which afforded exclusively 1,2-bisdiethylamino-3-chlorocyclopropenyl perchlorate (**54**). It was then demonstrated that these compounds were susceptible to oxidation to the corresponding radical dications. This was demonstrated by Yoshida and Gerson in 1971 by reacting the tris(dimethylamino)cyclopropenyl cation (**57**) with antimony pentachloride to afford **58** (Scheme 4), which was analyzed by electron paramagnetic (EPR) spectroscopy but could not be isolated.[73] Nevertheless, in 1975 Weiss reported a modified procedure for the synthesis of aminocyclopropenium radical dications, which were isolated and characterized.[74] At the time very little was known about radical dications. Given that a

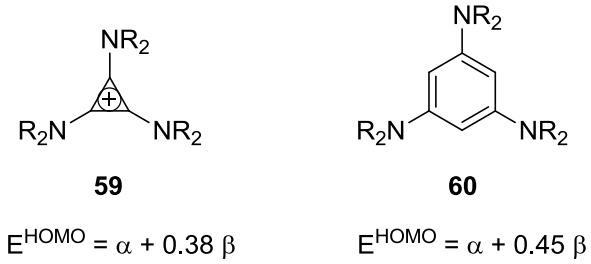
cationic molecule is by definition positively charged, removing an electron to afford a dication should not be a favorable process.

Scheme 4. Generation of triaminocyclopropenyl radical dications.



57 **58**

However, compounds of type **57** are actually electron rich, with high lying HOMOs. In fact, the HOMO of tris(dialkylamino)cyclopropenyl cation **59**, was found to be comparable to that of the degenerate HOMOs of neutral 1,3,5-tris(dialkylamino)benzene **60** (Figure 15).



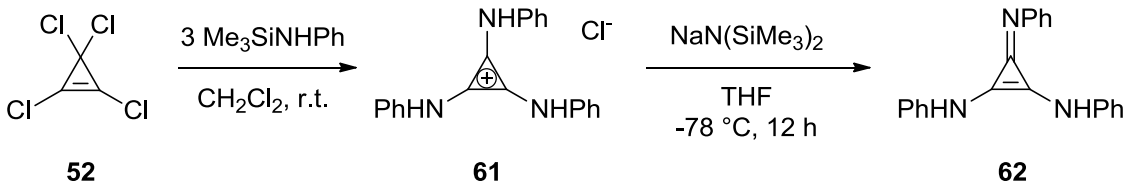
59 **60**

$E^{HOMO} = \alpha + 0.38\ \beta$ $E^{HOMO} = \alpha + 0.45\ \beta$

Figure 15. The HOMO orbital energy coefficients derived from Huckel's HMO method for tris(dialkylamino)cyclopropenyl cation **59** and 1,3,5-tris(dialkylamino)benzene (**60**).

In 1979 Weiss reported the selective synthesis of previously inaccessible mono- and bis-aminocyclopropenimines using trimethylsilyl amines by simple variation of temperature and stoichiometry.[75] The following year Weiss used this methodology to synthesize, what he termed, "*an aza-analogue of deltic acid"* (**62**, Scheme 5) by employing *N*-trimethylsilyl aniline to yield **61**, followed by deprotonation with sodium bis(trimethylsilyl)azide.[76] This represented the first synthesis of a neutral trisaminocyclopropenimine.

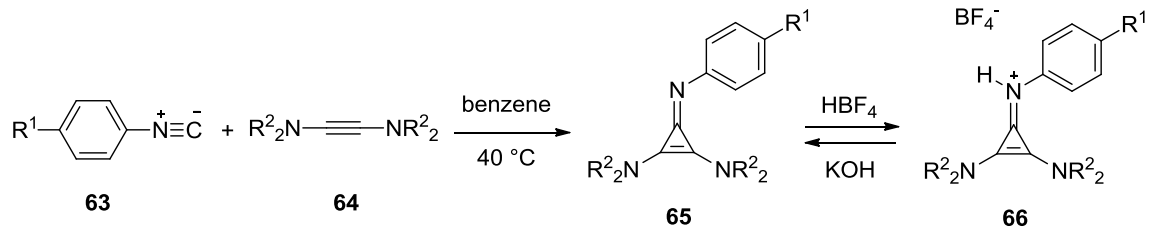
Scheme 5. Weiss's synthesis of an aza-anologue of deltic acid (**62**).



52 **61** **62**

The second reported synthesis of a bis(dialkylamino)cyclopropenimine occurred in 1984,[77] when Krebbs described the addition of isocyanides across aminoalkynes to yield the corresponding cyclopropenemines (Scheme 6).

Scheme 6. Krebbs' general cyclopropenimines synthesis using alkynes and isocyanates.



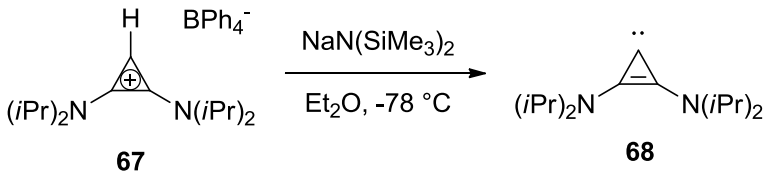
63 **64** **65** **66**

R^1 = NO_2, CN, Cl, H, CH_3, OCH_3, $N(CH_3)_2$

R^2 = CH_3, C_2H_5

It was also around this time that Yoshida reported the synthesis of a hydrogen substituted bis(dialkylamino)cyclopropenium derivative (**67**, Scheme 7).[78] This work became particularly relevant in 1985 when the cyclopropenylidene (C_3H_2) cation was discovered in interstellar space, characterized by comparing astronomical radio lines to ab initio calculations.[79] This small organic molecule was found to be extremely prevalent in interstellar space,[80] though it was generally believed to be too unstable for laboratory isolation. Nevertheless, two decades after its discovery, Bertrand reported the synthesis, isolation, and characterization of cyclopropenylidene **68** in 2006 (Scheme 7).[81]

Scheme 7. Bertrand's synthesis of cyclopropenylidine, **68**.



Bertrand's efforts were based on previous theoretical considerations suggesting that the rearrangement of cyclopropenylidenes to other molecular entities was not kinetically favorable, and should thus be sufficiently stable for laboratory isolation. As such, he sought to convert the known, stable, cyclopropenium tetraphenylborate cation **67** to the corresponding cyclopropenylidene, **68**. This was successfully accomplished by reacting bis(diisopropylamino)cyclopropenium tetraphenylborate with potassium bis(trimethylsilyl) amide, followed by a slow addition of dry diethyl ether at -78°C. Though sensitive to moisture and air oxidation, **68** was found to be sufficiently stable for isolation and X-ray diffraction analysis, which was used to confirm its molecular identity. While screening counterions for stability, Bertrand noted[82] that alkyl lithium bases were not suitable for the generation of these compounds: The isolation of cyclopropenylidenes would likely have come much earlier had Weiss[83] employed a base other than *n*-BuLi. Bertrand's work established the stability of cyclopropenylidines, and their existence as carbenes.

Following Bertrand's work, in 2010 Alcarazo evaluated the application of cyclopropenylidenes as a ligand for N(1)-complexes, which he used as metal chelating ligands (Figure 16).[84]

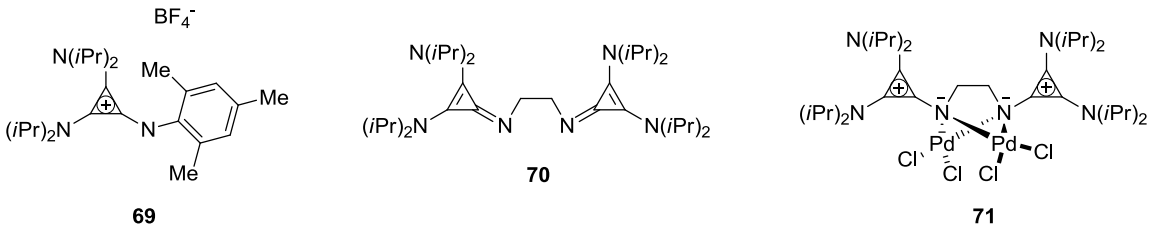
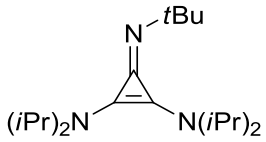


Figure 16. Alcarazo's cyclopropenimine containing N(1)-based ligands.

This included the first bidentate bis-bis(dialkylamino)cyclopropenimine compound (**70**), which was found to react with two equivalents of $[PdCl_2(CH_3CN)_2]$ to yield complex **71**. Complex **71** possessed a highly unique geometry, owing to the donation of four electrons from each central N-atom, which resulted in an unprecedented bis-metalated complex. The following year Alcarazo then expanded this work by reporting cyclopropenylidines ligated to phosphorus.[85] Meanwhile, Curnow et al. reported the application of the related triaminocyclopropenium salts as ionic liquids.[86] These salts were thermally stable, air and moisture sensitive, easy to synthesize, possessed low melting points and valuable electrochemical properties and good viscosity. Continuing the surge in cyclopropenimine related chemistry, in 2012 Lambert et al. reported the first pK_a measurement of a bis(amino)cyclopropenemine.[87] The pK_a of cyclopropenimine **72** (Figure 17) was measured in MeCN using NMR exchange experiments, and was discovered to be only 0.08 pK_a units lower than Schwessinger's P1 base (**8**).



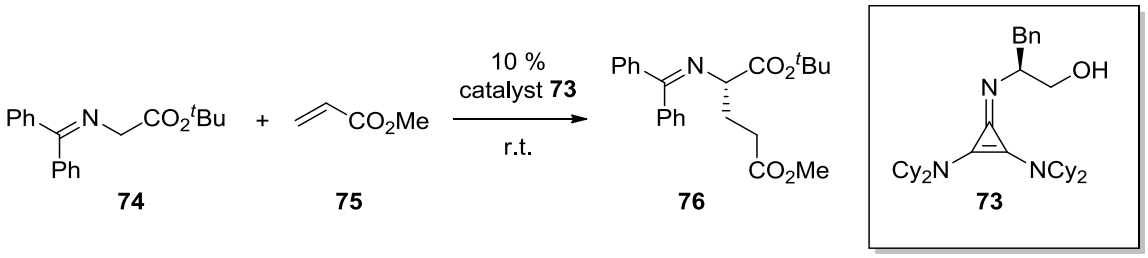
72

$pK_{a(MeCN)} = 26.9$

Figure 17. First pK_a measurement of a cyclopropenimine.

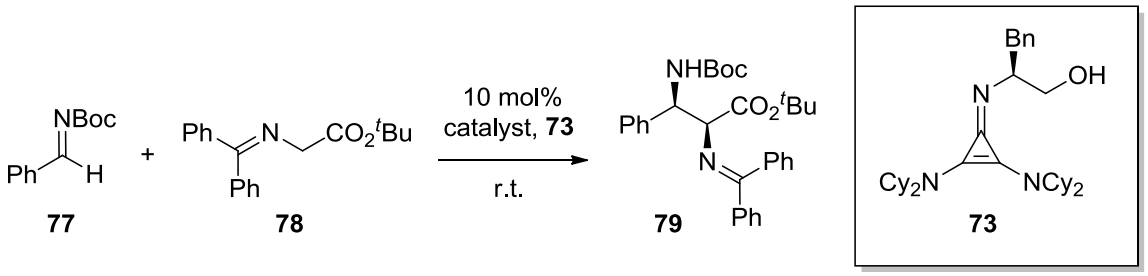
Futhermore, this report demonstrated an efficient, multi-gram scale synthesis of an amino acid substituted cyclopropenimine (**73**) and its application as a Brønsted base catalyst for an asymmetric Michael addition (Scheme 8), thus marking the beginning of cyclopropenimine catalysis. The authors were able to obtain yields and enantioselectivities as high as 99% using only 10 mol % of catalyst **73**.

Scheme 8. Enantioselective Michael addition catalyzed by a chiral cyclopropenimine.



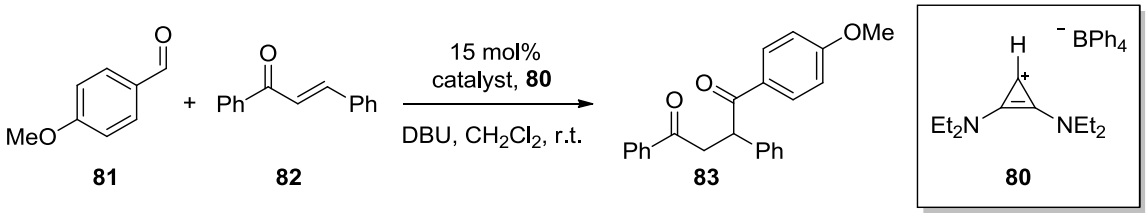
In 2013 Lambert extended his work by applying the same chiral cyclopropenimine catalyst to an enantioselective Mannich reaction (Scheme 9).[88] Therein, he was able to demonstrate that catalyst **73**, at only 1 mol %, provided greater yields of **79** than the widely used thiourea cinchona alkaloid-derived catalysts, while maintaining excellent levels of enantio- and diastereoselectivity. Furthermore, the catalyst was found to be highly functional group tolerant and compatible with large scale reactions.

Scheme 9. Enantioselective Mannich reaction catalyzed by a chiral cyclopropenimine.



Shortly thereafter, Gravel reported the use of bis(dialkylamino)cyclopropenyl cation, **80**, as an organocatalyst in the Stetter reaction (Scheme 10).[89] Gravel employed DBU as an auxiliary base to generate the corresponding bis(dialkylamino)cyclopropenylidine, as the active catalyst, *in situ*, which was found to provide better yields and cleaner reactions than the two most commonly used NHCs without formation of benzoin by-products.

Scheme 10. bis(dialkylamino)cyclopropenylidine catalyzed Stetter reaction.



Lastly, the broader utility of catalyst **80** was demonstrated recently, with Anand's report of cyclopropeneylidine catalyzed 1,6-conjugate additions for the synthesis of diarylated ketones.[90]

1.5 – Research Goals and Objectives

The overarching goal of this work is to cultivate a more comprehensive understanding of the hydrogen bonding abilities and electronic nature of cyclopropenimines as a means to facilitate a longer-term agenda of rationally designing new catalysts, ligands, and materials. Specifically, we sought to investigate the nature of cyclopropenimine hydrogen bonding and aromaticity within the proton sponge backbone using experimental, physical organic, and computational techniques. The traditional proton sponge backbone was chosen because it is relatively simple, structurally rigid, and well-studied, and thus the

results can thus be easily compared with those of other proton sponge derivatives and hydrogen bond donor/acceptors.

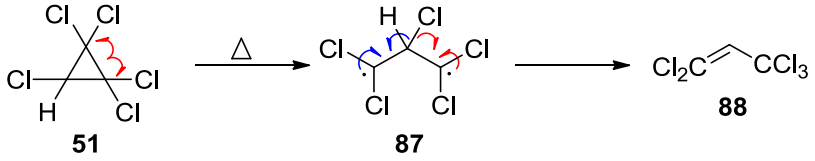
Chapter 2 - Results and Discussion

2.1 - Generating tetrachlorocyclopropene

Given the research theme, a continuous supply of tetrachlorocyclopropene was required for the synthesis of cyclopropenimine-substituted proton sponges. The most practical approach to its synthesis was developed by Stephen W. Tobey during his Ph.D. work at the University of Wisconsin in 1965 under Robert West.[69] The reaction involved generating dichlorocarbene in a solution of trichloroethylene using a small amount of l,2-dimethoxyethane as a catalyst (Scheme 2). Prior to the development of this methodology, Seyferth and Burlitch were able to obtain *gem*-dihalocyclopropanes (including trichlorocyclopropene)[91] in far greater yields by reacting phenyl(trihalomethyl)mercurials with olefins. However, Tobey and West chose not to use this protocol on account of the expense and toxicity of the reagents. Instead, they chose to apply Wagner's procedure,[68] which involved much less toxic reagents that are cheaper and more readily available. A slight modification to Tobey and West's synthesis of pentachlorocyclopropane came in 1975 when Sepiol and Soulen discovered a two-fold increase in yield by simply halving the amount of 1,2-dimethoxyethane.[92] The argument used by the authors was that generating the carbene at a slower rate diminishes the frequency of side reactions and accompanying by-products. Though this procedure is effective, several significant drawbacks still exist, including the long reaction times (> 72 hours) and the necessity for

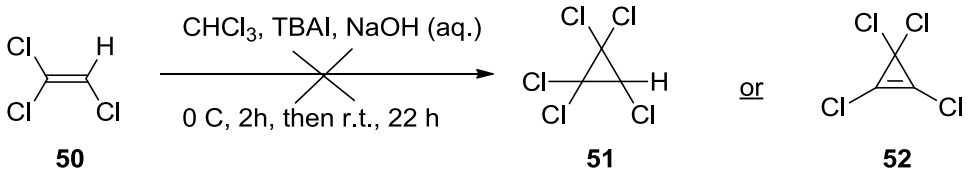
strict temperature control. The reaction mixture must be kept above 90 °C for product formation, and below 100 °C to prevent homolysis of the CCl_2—CCl_2 bond (Scheme 11) and its subsequent rearrangement to alkene **88**. In addition, the maximum yield obtained with this procedure, after the target compound was purified by distillation, was 42 %.

Scheme 11. Thermal rearrangement of pentachlorocyclopropane to 1,1,3,3,3-pentachloropropene.



A number of new cyclopropanation reactions and protocols have since been developed and their application to the synthesis of pentachlorocyclopropane was investigated in an effort to improve the synthesis of **51** and **52**. In 1999, a new phase transfer catalyst was developed for the addition of dichlorocarbene to alkenes.[93] Though the reported catalyst showed marked improvement on traditional phase transfer agents, traditional catalysts such as tetrabutylammonium iodide (TBAI) were still effective. This procedure was adapted for the synthesis of **51** (Scheme 12). It was hypothesized that in the presence of a phase transfer catalyst, NaOH would deprotonate chloroform to afford dichlorocarbene, which would in turn insert into the double bond of trichloroethylene to yield **51**.

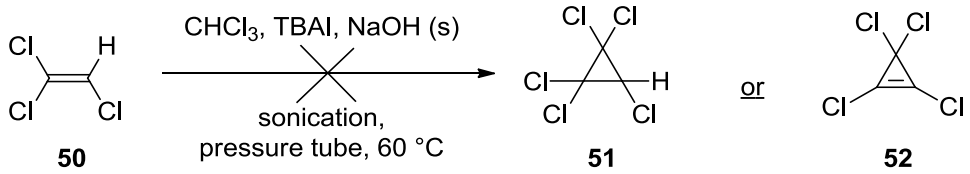
Scheme 12. Phase transfer approach to the synthesis of tetrachlorocyclopropene, **51**.



Unfortunately, the crude ^{1}H NMR spectrum did not show a signal for the lone proton of **51**. Given the presence of concentrated NaOH in the reaction, it was postulated that perhaps **52** was being generated *in situ*. However, a crude IR spectrum of the resulting

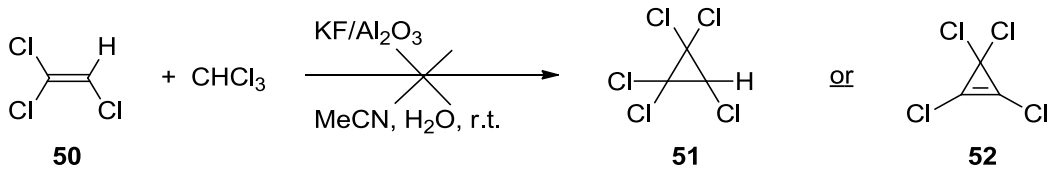
reaction mixture showed no evidence of **52**. As such, a modified procedure was attempted based on the work of Molinski et al.,[94] employing anhydrous conditions, powdered NaOH, and sonication of the reaction mixture in a sealed pressure tube (Scheme 13).

Scheme 13. Alternative phase transfer approach to the synthesis of tetrachlorocyclopropene, **51.**



However, immediately upon addition of powdered KOH to the reaction vessel, the formation of smoke, bubbles, and effervescence was observed. The fume hood was quickly closed for precaution, at which point a loud bang was heard, followed by the eruption of the reaction mixture from the vessel (not unlike an explosion). The aftermath was a smouldering, foul-smelling, black tar, which upon ^{1}H NMR analysis, did not contain even trace amounts of **51**. In light of this outcome, a more recent approach developed in 2005 by Komatsu et al. was attempted.[95] Once again, the reagents were adjusted for the synthesis of **51** (Scheme 14). A combination of potassium fluoride and aluminum oxide was added to a solution of **50** and chloroform in MeCN and water at room temperature.

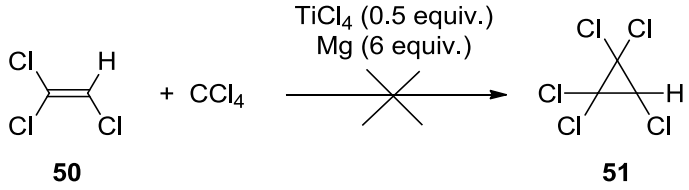
Scheme 14. New synthetic approach to the synthesis of tetrachlorocyclopropene, **51**.



Unfortunately, the resulting crude ^{1}H NMR spectrum showed no evidence that **51** was formed in the reaction. The inability of these three procedures (Schemes 12-14) to afford any observable product formation is possibly an indication that **51** should not be generated under basic conditions. One explanation for the lack of observed product is that under the reaction conditions **51** and **52** may both be too reactive to be observed. For instance, **51** can rapidly react to form **52**, which itself is a more reactive substrate for cyclopropanation.

A final alternative approach to the synthesis of **51** was endeavoured, which did not require basic conditions. The procedure was based on that reported by Yan and coworkers in 2006 (Scheme 15)[96] which uses $TiCl_4$ and Mg to generate dichlorocarbene. It, too, was adapted for the synthesis of **51** and once again, was unsuccessful. In this instance, it is likely that excess Mg would be prone to C-Cl insertion into both **50** and **51**, which would lead to a number of undesired by-products.

Scheme 15. New synthetic approach to the synthesis of tetrachlorocyclopropene, **51**.



50 **51**

It is likely that the reaction scheme shown in Scheme 15

Though reaction conditions were not by any means exhaustively screened for the described alternate methods for the synthesis of **51** (Schemes 12 -15), it was pertinent to move forward with the intended research and thus **51** was made using the existing method of Tobey and West.

2.2 - The 1,8-Bis(bis(diisopropylamino)cyclopropeniminyl)naphthalene Proton Sponge, DACN

At the outset of this thesis work in 2012, interest in cyclopropenimines was only just emerging. Given the Dudding group's existing interest in hydrogen bonding, we saw the opportunity to investigate the hydrogen bonding properties of cyclopropenimines through the geometrical constraints of a proton sponge backbone. It was also envisioned that a cyclopropenimine substituted proton sponge (**89**, Figure 18) would constitute a neutral, organic superbase that could potentially rival the strongest existing bases of this type. Furthermore, the synthesis of a cyclopropenimine substituted proton sponge was seen as an interesting amalgamation of two historically relevant molecules and would be of great theoretical interest. Such a proton sponge derivative would introduce a new influencing factor on the basicity of the proton sponge, namely the generation of aromaticity upon protonation.

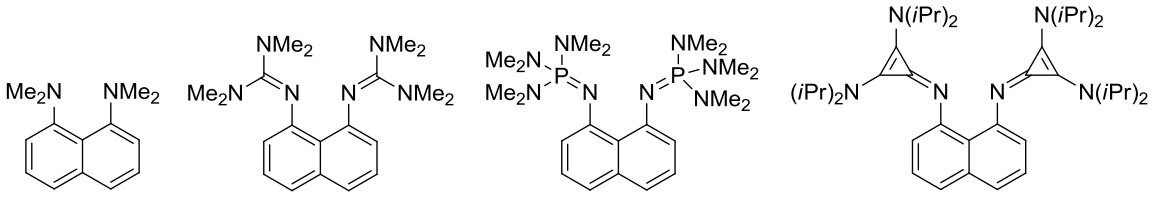
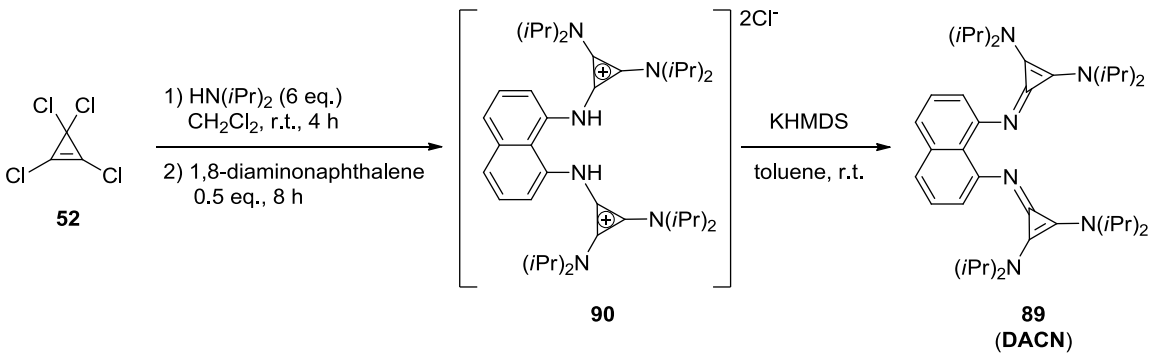


Figure 18. Selected examples of various *N*-susbtituted proton sponges.[41,44,24,97]

The synthesis of the aforementioned cyclopropenimine substituted proton sponge, 1,8-bis(bis(diisopropylamino)cyclopropeniminyl)naphthalene (**89**), is outlined in Scheme 16. Under a dry, inert atmosphere, a solution of tetrachlorocyclopropene (**52**) in dichloromethane (DCM) was reacted with excess diisopropylamine, followed by the addition of half an equivalent of 1,8-diaminonaphthalene.

Scheme 16. Synthesis of 1,8-bis(bis(diisopropylamino)cyclopropeniminyl)naphthalene, **89**.



The product of this reaction is the di-hydrochloride salt, **90**, which is a solid and varied in colour between different shades of red, purple, and brown. Even after purification by column chromatography, significant colour remains despite the absence of any by-products by ^{1}H-NMR or ^{13}C-NMR. However, re-crystallization afforded colourless crystals, indicating that the initial colour is not an inherent property of **90**. Further evidence to this fact comes from the slight increase in melting point after successive crystallizations. Re-crystallization was not a trivial task. After numerous attempts, the only effective method of crystallization (discovered fortuitously) was a vapour diffusion crystallization. In a 10 mL vial, **90** was dissolved in a 1:2 mixture of acetonitrile/benzene. The vial was placed in a beaker containing benzene which was then covered with aluminum foil. The chamber was allowed to stand until the solvent in the vial evaporates (approximately 72 hours), at which point a layer of white crystals had formed above a dark brown amorphous solid. The upper layer of colourless crystals were then removed and placed in another vial for further recrystallization. Three to four repetitions of this process were required to obtain colourless/white, needle-like crystals. These crystals were of sufficient purity to re-crystallize into single crystals from a 2:1 mixture of ethyl acetate/acetonitrile under traditional vapour diffusion technique (crystal formation takes

24-48 hours). This method provided relatively large, clear, colourless, single crystals. Synthesis of the **89** was achieved from deprotonation with potassium bis(trimethylsilyl)amide (KHMDS). It was also found that **90** may be deprotonated using concentrated KOH, though in lower yields than with KHMDS. Employing NaH in THF resulted in only minor product formation. Nevertheless, the product was readily obtained in three steps from inexpensive, commercially available starting materials to afford a bench stable solid. A counterion exchange was performed using $NaBF_4$ in dichloromethane. There were no noticeable physical changes when compared to the bis-HCl salt, though the bis-BF_4^- salt was slightly easier to crystallize. Multiple attempts were made to obtain a monoprotonated salt. Addition of one equivalent of KHMDS in toluene afforded either an intractable mixture of products, isolation of **89**, or isolation of **90**. The reverse process was also performed, wherein one equivalent of NH_4PF_6 was added to a solution of **89**. Surprisingly, when this experiment was repeated in an NMR tube, only the bis-protonated salt, **90**, and the freebase, **89**, were observed. One possible explanation for the difficulty in isolating a monoprotonated species is that its geometry possesses substantial steric repulsion resulting from the alignment between the cyclopropenimine rings and the naphthalene backbone, causing any monoprotonated compound to rapidly di-protonate.

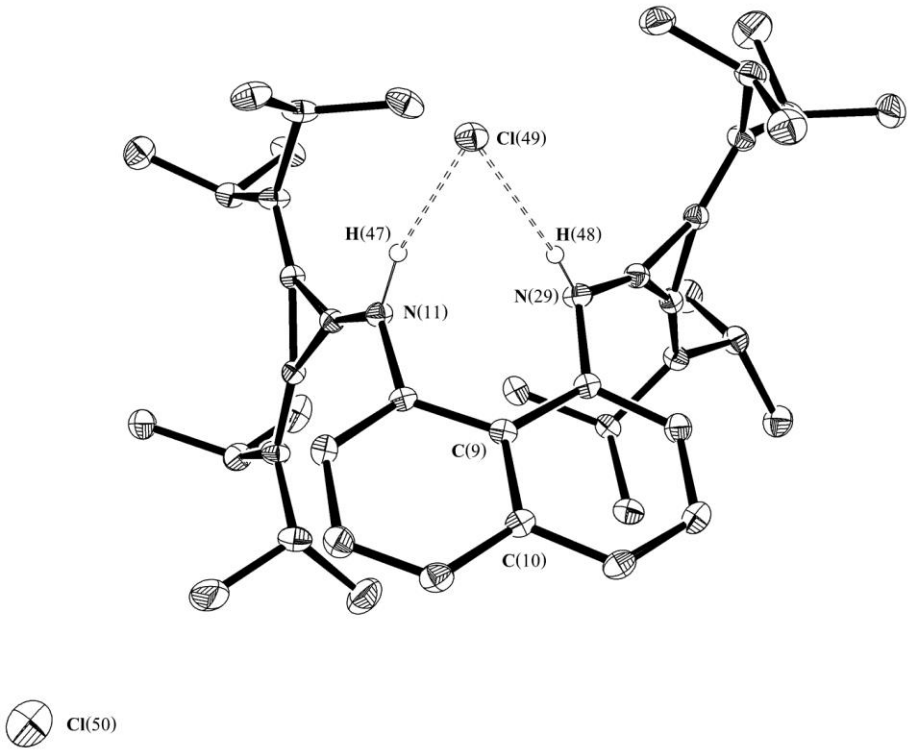


Figure 19. Ortep3 generated X-ray structure of bis-protonated **90**. Thermal ellipsoids are displayed at 50% probability. Solvent molecules, hydrogen atoms, and water have been removed for clarity (crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC 945116).

A single crystal of **90** was analyzed by X-ray diffraction. The crystal structure of **90** is shown in Figure 19, and a numbering scheme is presented in Figure 20a. The molecular structure of **90** possesses several notable features. First and foremost is the noticeable deviation in the torsion angles between cyclopropenyl rings and the naphthalene backbone as defined by the dihedral angles $\theta_{(9\text{-}8\text{-}11\text{-}12)}$ = 153.0°, and $\theta_{(9\text{-}1\text{-}29\text{-}30)}$ = 112.3°. What is more, both cyclopropenyl rings reside on the same face of the naphthalene ring system, resulting in a highly congested geometry, with C-N-C angles, $\phi_{(1\text{-}29\text{-}30)}$ and $\phi_{(8\text{-}11\text{-}12)}$, of 119.8° and 122.4°. Furthermore, the angles of the planes containing rings C and D with respect to the plane of the naphthalene backbone were similar (75.4° and 71.8°, respectively, Figure 20b) and the two N-H protons in this

complex are both coordinated to a nearby chloride ion (H(47)-Cl(49) = 1.15 Å, H(48)-Cl(49) = 1.38 Å). The second counterion was found to be chloride (Cl(50)) in 70% of the lattice, and hydroxide in the remaining 30%. Regardless, the second chloride counterion, Cl(50), is highly solvated by water and resides well outside the parent complex. The closest distance was 3.73 Å from the hydrogen atom residing on C(3), which is substantially greater than the sum of their van der Waals radii (H = 1.20 Å, Cl = 1.75 Å).[98] This relationship is reminiscent of a strained ion pair[99] resulting from interactions between dialkylamino-substituted cyclopropenyliums, which are electron-rich,[100] and electron-rich halides. As such, the "donor" cyclopropenylium ion in **90** may have a high-lying HOMO, despite the presence of a positive charge. Compound **90** therefore may be regarded as a "donor-donor" system, which should have "ion pair strain" (*i.e.*, a strong closed-shell repulsion between the electron-rich components), resulting in a "naked anion".

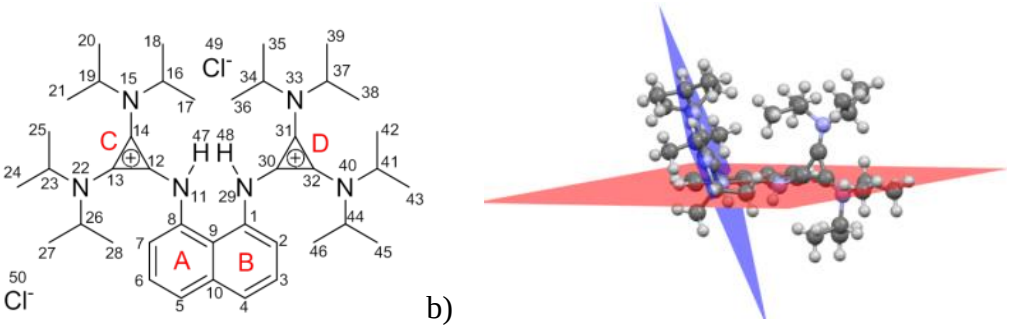


Figure 20. Bis-protonated **90**. (a) Atom and ring labelling (b) Mercury generated image of the angle made between the plane containing cyclopropenyl ring D (blue) and the plane containing naphthalene ring A/B (red).

Variable temperature (VT) ^{1}H NMR experiments were performed on the bis-protonated BF_4^- salt (**90•BF$_4$**), primarily to investigate the environments of the acidic protons H(47) and H(48). The VT experiment revealed that the N-H signals of H(47) and H(48) (@ ~

10.5 ppm) coalesced at a temperature of -45 °C (Figure 21). Below this temperature, the corresponding proton signals are separated by 1.5 ppm, which when compared with the 15 ppm shift reported recently by Pozharskii et al. for monoprotonated *N*,*N*,*N*'-trimethyl-1,8-diaminonaphthalene, is relatively small.[101] Regardless, it is unlikely that the observed 1.5 ppm shift difference results from the non-symmetric nature of **90•BF$_4$**. It is more probable that the peak separation is a result of two distinct proton environments, corresponding to H(47(a)) and H(48(a)) (see Figure 22, structure (A)). The rate constant (K_C) and activation barrier to this interconversion ($\Delta G^{\ddagger}$) were calculated to be ~1998 and ~10.4 kcal/mol, respectively, at -45 °C (see Appendix A for details).

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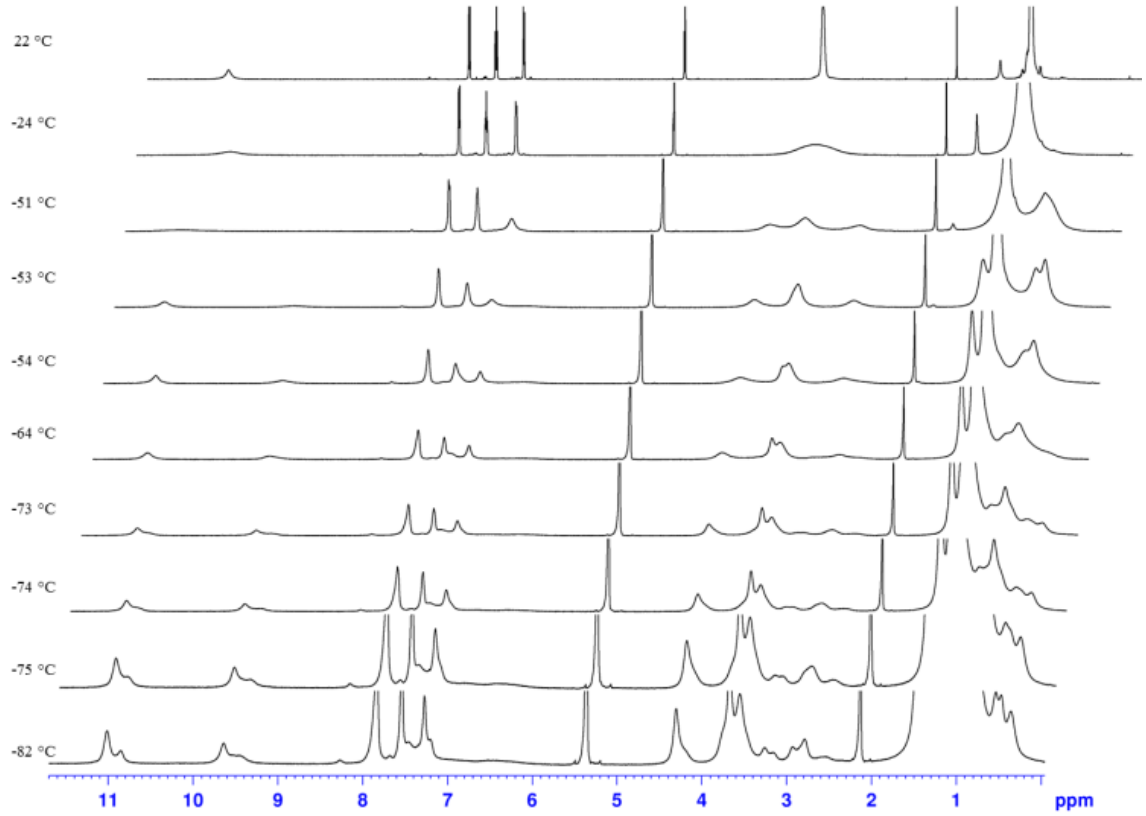


Figure 21. Variable temperature ^{1}H NMR spectrum (300 MHz) of **90**•BF_4 in CD_2Cl_2.

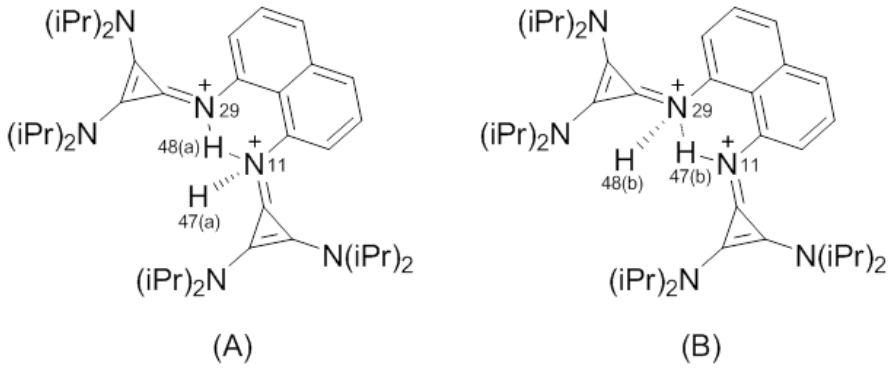
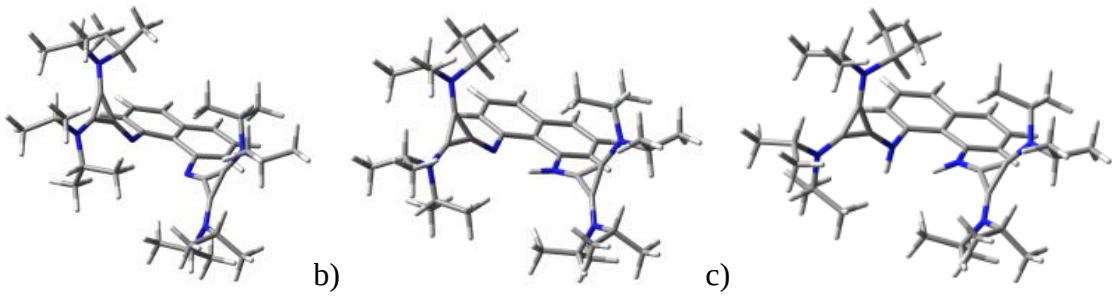


Figure 22. Possible explanation for the four distinct chemical shifts observed for H(47) and H(48) in **90•BF$_4$** below -70 °C.

Upon further cooling, as the temperature reached -70 °C the two N-H proton signals at 8.9 ppm and 10.4 ppm (H(47(a)) and H(48(a)) respectively) began to split further, indicating the existence of four distinct proton signals, likely arising from the non-symmetric nature of **90•BF$_4$**, which renders H(47(a)) and H(48(a)) (Figure 22, structure A) magnetically inequivalent from H(47(b)) and H(48(b)) (Figure 22, structure B), below -70 °C. The rate constant (K_C) and activation barrier to this interconversion ($\Delta G^{\ddagger}$) were calculated to be ~210 and ~10.2 kcal/mol, respectively, at -70 °C. There also appeared to be a strong correlation between H(47) and H(48) with the *ortho*-protons on C(2) and C(7) (7.2 ppm), which also split into two, and subsequently four signals as the sample was cooled.

To gain insight into the structural and electronic features of **89**, **90**, and the elusive monoprotonated species **91,** DFT calculations were performed at the IEFPCM/B3LYP/6-31G(d,p) level (acetonitrile, ε = 35.5). The resulting minima, which were confirmed by the presence of only real vibrational frequencies, are shown in Figure 23.



a) b) c)

Figure 23. IEFPCM /B3LYP/6-31G(d,p) (acetonitrile, Ɛ = 35.5) calculated structures of (a) **89**, (b) **91**, and (c) **90**.

The neutral species, **89**, is a highly strained molecule, as seen by the twisted naphthalene backbone, and the distortion of N(11) and N(29) from the plane of the naphthalene ring system (*Table 1*). This distortion originates predominantly from avoidance of unfavourable steric contacts between the diisopropyl groups of the two cyclopropenyl ring systems, and minimization of N_{LP}-N_{LP} repulsion. The minimization of N_{LP}-N_{LP} repulsion is apparent from a large N(11)-N(29) interatomic distance of 2.84 Å (*Table 2*), the N(11) and N(29) out-of-plane distortion from the naphthalene plane, evident from the dihedral angles $\varphi_{(11\text{-}8\text{-}9\text{-}10)}$ = 15.2° and $\varphi_{(29\text{-}1\text{-}9\text{-}10)}$ = 6.0°, and the degree of twisting within the naphthalene ring system defined by the angle $\Psi_{(1\text{-}9\text{-}10\text{-}5)}$, which deviates by 6.7° from ideal planarity. Additionally, the angles between the cyclopropenyl rings (*Table 1*), and the naphthalene backbone of 68° and 52° are such that they allow simultaneous orbital overlap with the nitrogen lone pairs.

Table 1. Selected Angles in **89**, **91**, and **90.**

	$\theta_{(9\text{-}8\text{-}11\text{-}12)}$	$\theta_{(9\text{-}1\text{-}29\text{-}30)}$	$\phi_{(8\text{-}11\text{-}12)}$	$\phi_{(1\text{-}29\text{-}30)}$	$\Psi_{(1\text{-}9\text{-}10\text{-}5)}$
89	148.8°	143.8°	123.1°	119.2°	173.3°
91	151.6°	152.4°	123.1°	119.0°	179.5°
90	160.8°	136.0°	125.0°	120.9°	177.0°
	$\varphi_{(10\text{-}9\text{-}8\text{-}11)}$	$\varphi_{(10\text{-}9\text{-}1\text{-}29)}$	**< AB-C**	**< AB-D**	
89	164.8°	174.0°	68.4°	52.1°	
91	178.2°	175.5°	68.2°	55.0°	

90	175.1°	173.0°	53.6°	73.0°

On the other hand, monoprotonated species **91** possesses an IHB (N(29)-H(47) = 1.80 Å), which alleviates the N_{LP}-N_{LP} repulsion present in **89** and decreases the N(11)-N(29) interatomic distance to 2.67 Å. The presence of an IHB was supported by a donor-acceptor interaction (E_{NBO} = 20.1 kcal/mol) in the context of natural bond orbital (NBO) theory and by a bond critical point in the context of Bader's theory of Atoms in Molecules (AIM) (see Appendix A for a brief description of NBO and AIM theory, as well as the computed AIM structure of **89**, **91**, and **90**). Evidence of the relief of strain upon protonation of **89** is observed in the increased planarity of the naphthalene ring system in **91** ($\Psi_{(1\text{-}9\text{-}10\text{-}5)}$ = 179.5), with N(11) and N(29) becoming almost perfectly aligned. Protonation of N(11) also results in an increased N(11)-C(12) bond distance, and a decreased $N(11)_{LP}$ donation into the cyclopropenyl ring system (*Table 3*), associated with an increased aromaticity in the cyclopropenyl ring.

In terms of bis-protonated **90**, the computed structure shows a significantly weakened IHB relative to **91** (N(29)-H(47) = 2.13 Å, E_{NBO} = 4.7 kcal/mol), which results in elongation of the N(11)-N(29) interatomic distance to 2.82 Å (*Table 2*), similar to that found in the freebase **89**. Furthermore, as observed with protonation of N(11), the N(29)-C(1) and N(29)-C(30) bond distances increase upon protonation of N(29), indicative of increased polarization of the imine bond onto N(29), and formation of the cyclopropenylium cation.

Table 2. Selected bond distances (in Å) within **87**, **86**, and **88.**

	N(11)-N(29)	**N(11)-C(8)**	**N(29)-C(1)**	**N(11)-C(12)**	**N(29)-C(30)**
87	2.84	1.38	1.39	1.31	1.32
88	2.67	1.41	1.39	1.36	1.33

86	2.82	1.41	1.45	1.36	1.36

The NBO energies presented in Table 3 suggests that N(11) and N(29) possess lone pairs even after they have been protonated (*i.e.*, in **89**, **91**, and **90**). Additionally, in all three species the lone pairs of N(11) and N(29) are in simultaneous communication with the naphthalene backbone and the cyclopropenimine rings. The decreased lone pair donation into the adjacent cyclopropenyl ring with each successive protonation corresponds well with the observed increase in bond distance.

Table 3. Selected NBO donor-acceptor energies (kcal/mol) in **89**, **91**, and **90**.

NBO Interaction	**89**	**91**	**90**
$N(11)_{LP} \rightarrow$ BD* C(12)-C(13)	18.51	11.04	4.28
$N(29)_{LP} \rightarrow$ BD* C(30)-C(32)	18.58	14.38	1.40
$N(11)_{LP} \rightarrow$ BD* C(8)-C(7)	12.18	33.44	30.19
$N(29)_{LP} \rightarrow$ BD* C(1)-C(2)	6.78	6.32	5.87

* LP = lone pair. BD* = antibonding orbital.

The NBO data also reveals the presence of carbon lone pairs on C(12) and C(30) upon protonation of N(11) and N(29), respectively. These lone pairs reside in the sigma plane of rings C and D, to provide what in essence is a singlet carbene, that is, a *N*-centered cyclopropenylidene. Incidentally, these results coincide well with Bertrand's findings that bis(diisopropylamino)cyclopropenylidenes are isolable species in the laboratory,[102] and the observations of others that upon *N*-protonation of bis(dialkylamino)cyclopropenimines, the resultant cyclopropenylium cation can be regarded as a *N*-coordinated carbene ligand.[103] Lastly, the strong lone pair donation from N(11) and N(29) into the antibonding orbitals of C(8)-C(7) and C(1)-C(2) (*Table 3*), correlate well with their synchronized changes in chemical shift during the VT experiments.

The filled HOMOs of **89**, **91**, and **90** are shown in Figure 24, are of π-character, and are distributed over all four ring systems, as well as the N(11) and N(29) nitrogens. This delocalization of electron density is consistent with the abovementioned NBO data, indicating a large degree of N(11) and N(29) lone-pair donation into the adjacent aromatic ring systems. The LUMO shares many of the same traits as the HOMO in that it is delocalized over all four ring systems. Furthermore, the portion of the HOMO and LUMO residing on the naphthyl backbone of **89**, **91**, and **90** appears strikingly similar to what one would expect to find in the parent compound, naphthalene.

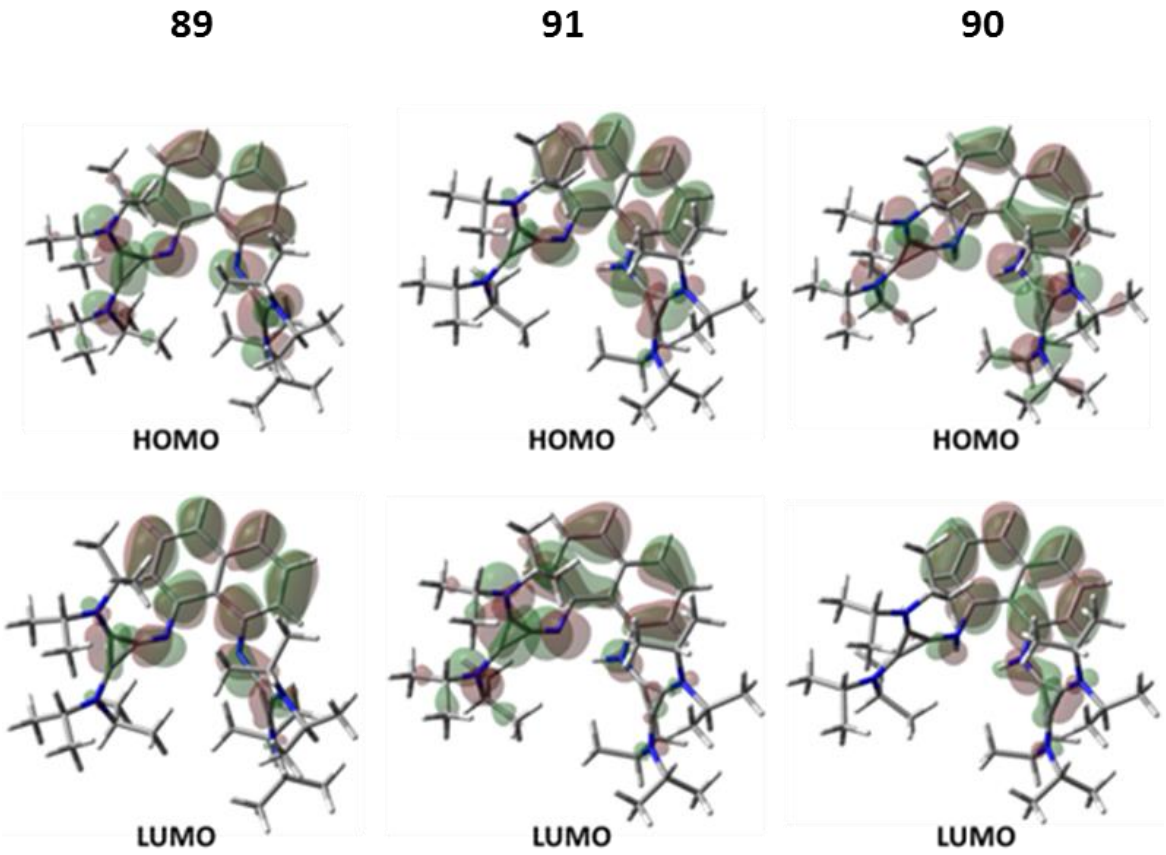
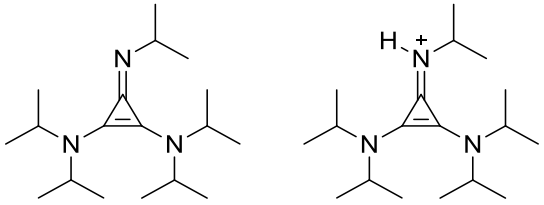


Figure 24. IEFPCM/B3LYP/6-31G(d,p) (acetonitrile, Ɛ = 35.5) calculated HOMOs and LUMOs of **89**, **91**, and **90**.

Nucleus independent chemical shift (NICS) calculations[104] were then performed on the four ring systems, A, B, C and D (see Figure 20a) of **89**, **91**, and **90** to investigate the changes in aromaticity, *i.e.*, the fourth factor attributing to the basicity of the proton sponge derivative. NICS calculations were developed by Schleyer et al. as a computational means to assess the extent of aromaticity within a ring. An aromatic system generates an external magnetic field, which would strongly affect the chemical shift of an atom at its center. This fact is exploited by placing a "ghost atom" (an atom with no mass or nuclear charge) at the geometric centre of a ring system and computing its chemical shift. The associated chemical shift will be directly proportional to the surrounding magnetic field, which is directly proportional to the extent of aromaticity of the ring system. Since this represented the first reported NICS calculation of a cyclopropenimine ring system, we first computed the corresponding NICS values of a representative model system, namely, *N*-isopropyl-bis(diisopropylamino)cyclopropenimine (**92**, Figure 25) and its protonated counterpart (**93**). Following the advancements in the theory and application of NICS, the NICS(0) values (computed at the centroid of the corresponding ring system) were accompanied by NICS(1) values, which are computed 1 Å above the ring's centroid. NICS(1) values are computed in order to minimize σ-contamination from the cyclopropenyl framework. Additionally, because of the unsymmetric chemical environments of these species, the corresponding NICS(1) values were computed 1 Å above and 1 Å below the NICS(0) values, herein termed NICS(1) and NICS(-1), respectively.



92 **93**

	92	**93**
NICS(-1)	8.27	9.51
NICS(0)	29.12	32.98
NICS(1)	7.82	9.11

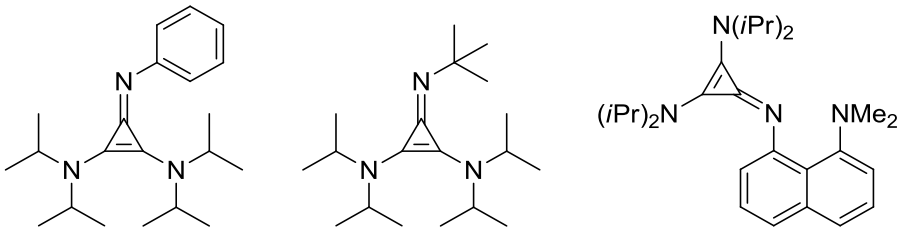
Figure 25. Computed NICS values for **92**, and **93**.

The σ-contamination arising from the cyclopropenium ring systems is clearly apparent from the large NICS(0) values computed for **92** and **93**. As expected, this contamination was avoided by computing NICS(1) and NICS(-1). Nevertheless, in all three NICS calculations an increase in chemical shift (and thus aromaticity) is observed upon protonation (i.e., the NICS(1) value of 7.82 for **92** increases to 9.11 in **93**). With this benchmark in mind, it is apparent from the NICS(0) and NICS(1) values for **89**, **91**, and **90**, shown in Table 4, that there is an increase in aromaticity within all four ring systems after each successive protonation (*i.e*, going from **89** to **91**, and **91** to **90**). With respect to the cyclopropenimine ring systems, the increased aromaticity in rings C and D accompanying protonation of N(11) and N(29), respectively, is attributed to the generation of the cyclopropenylium cation.

Table 4. B3LYP/6-311++G(d,p)// B3LYP/6-31G(d,p) calculated NICS(-1), NICS(0), and NICS(1) values for **89**, **91**, and **90**. (See Figure 20 for nomenclature)

		89	**91**	**90**
Ring A	**NICS(-1)**	8.48	9.30	7.99
	NICS(0)	6.78	7.81	8.51
	NICS(1)	7.99	9.03	10.20
Ring B	**NICS(-1)**	7.72	8.97	10.03
	NICS(0)	6.69	8.23	8.62
	NICS(1)	8.38	9.28	10.56
Ring C	**NICS(-1)**	9.08	9.02	8.69
	NICS(0)	30.64	30.10	31.23
	NICS(1)	8.20	8.45	9.45
Ring D	**NICS(-1)**	8.48	9.01	8.89
	NICS(0)	29.12	29.70	32.24
	NICS(1)	7.87	8.12	9.35

The gas-phase proton affinity (PA) of **89** was next calculated, which is a measure of a molecule's basicity in the gas phase and is equal to the energy released upon protonation (*i.e.*, the calculated energy difference between a molecule and its protonated counterpart). The PA of **89** was computed at the B3LYP/6-311G++(d,p)//B3LYP/6-31G(d,p) level, taking into account thermal corrections estimated by the B3LYP/6-31G(d,p) method, and was determined to be 282.3 kcal/mol. For comparison, the PA of *N*-Ph-bis(diisopropylamino)cyclopropenimine (**94**, Figure 26), *N*-*tert*-Bu-bis(diisopropylamino)cyclopropenimine (**72**), and a proton sponge derivative bearing one NMe_2 group and one cyclopropenimine substituent (**95**) were computed at the same level of theory.



94 **72** **95**

Figure 26. Structures of **72**, **94**, and **95** for comparison of PA**.**

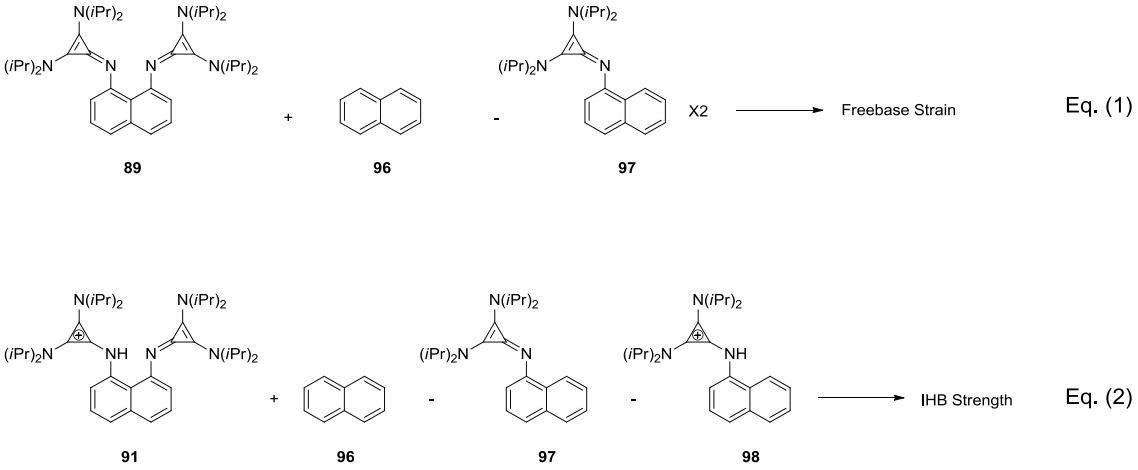
The corresponding proton affinities were calculated to be 260.1 kcal/mol, 266.0 kcal/mol, 266.8 kcal/mol, respectively, for **94**, **72**, and **95**. The lower PA associated with **94** (relative to **72**) is an expected consequence of the electron withdrawing phenyl substituent. Furthermore, the modest increase in PA in moving from **72** to **95** likely arises from destabilization of the freebase, commonly associated with proton sponges. Perhaps more importantly is the comparison between **89** (PA = 282.3 kcal/mol) and **95** (PA = 266.8 kcal/mol), which suggests that both cyclopropenimine units of **89** contribute to its basicity.

With respect to the concept of pK_a, using the polarized continuum solvation model (acetonitrile, Ɛ = 35.5), and TMGN (**34**) as a reference base (pK_a = 25.1[105]), the pK_a of **89** was computed at the B3LYP/6-31G(d,p) level to be 27.0 (See Appendix B for details on the calculation of pK_a). When this value is compared to that of cyclopropenimine **72** (pK_a = 26.9 [53a]), it would appear that the proton sponge backbone of **89** imparts only a minor increase in basicity.

Homodesmotic reactions[106] were used in order to estimate the factors contributing to the strong PA predicted for **89**. The homodesmotic reations shown in Equations (1) and (2) were considered (Scheme 17). These homodesmotic reactions demonstrate the contribution of repulsive interactions in the neutral base (Equation 1), and the IHB

strength in the protonated species (Equation 2). The strain in the neutral base associated with steric and lone pair repulsion was 21.1 kcal/mol, while the IHB was calculated to be 1.2 kcal/mol. Accordingly, this data suggests that the extremely high PA predicted for **89** is almost entirely a consequence of a destabilized neutral species, while only a small contribution is provided by the IHB.

Scheme 17. Homodesmotic reactions calculated at the B3LYP/6-31G(d,p) level to demonstrate the contribution of repulsive interactions in the neutral base (Eq. (1)), and the IHB strength (Eq. (2)) to the PA of **89**.



In summary, the synthesis and characterization of a new proton sponge derivative, 1,8-bis(bis(diisopropylamino)cyclopropeniminyl)naphthalene **89** (**DACN**), as well as its bis-protonated counterpart **90**, have been reported. A crystal structure of **90** is presented, along with variable temperature ^{1}H NMR data on the BF_4^- salt (**90•BF_4**). DFT calculations were performed to investigate the structure of the monoprotonated species **91** and to gain insight into its structural and electronic nature. The PA of **89**, calculated at the B3LYP/6-311G++(d,p)//B3LYP/6-31G(d,p) level, taking into account thermal corrections estimated by the B3LYP/6-31G(d,p) method, was 282.3 kcal/mol, while its pK_a was estimated at 27.0. NICS calculations were performed to examine the changes in aromaticity within these systems upon successive protonations. Lastly, homodesmotic reaction schemes were used in order to estimate the factors contributing to the strong PA predicted for **89**.

2.3 - Application of DACN-2HCl as a phase transfer catalyst:

Shortly after the results of **DACN** were published,[97] a colleague in the Dudding group synthesized cyclopropenimine derivative **99** (Figure 27) and subsequently demonstrated its application as a phase transfer catalyst (PTC) for benzylation and fluorination reactions.[54a] This result marked the first example of a DAC-based phase transfer catalyst. From an experimental standpoint, phase transfer protocols are particularly advantageous as they are in general operationally simple, amenable to both large and small scale synthetic protocols, involve mild reaction conditions, and use inexpensive reagents and solvents. As a result, it is perhaps not surprising that the scope of phase transfer chemistry has continued to grow at an accelerated pace, resulting in a

number of catalysts and protocols for phase transfer reactions with distinct modes of catalysis.[107] Recently, building upon earlier works exploring multi-site PTCs (catalysts with more than one active site),[108] particular emphasis has been placed on bifunctional catalysts combining both hydrogen bonding and phase transfer motifs.[109] Among this class of PTCs, combining positively charged quaternary ammonium cations as the phase transfer functionality and urea or thiourea as the hydrogen bond donor is the most predominant approach.

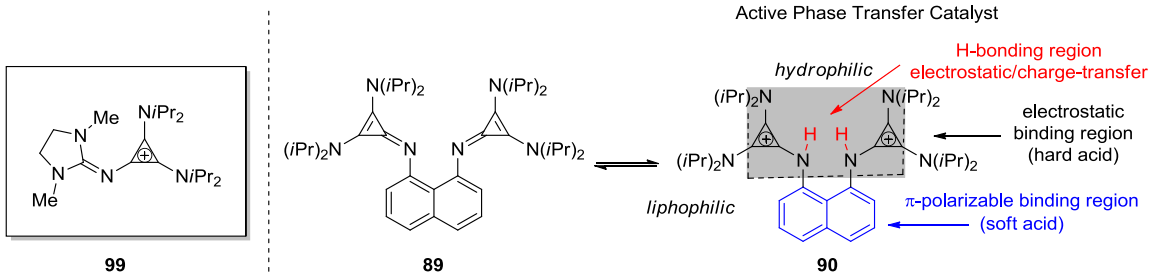


Figure 27. Recently Reported Cyclopropenimine Compounds, **99**, **89**, and **90**.

As part of our continued interest in phase transfer reactions and hydrogen bonding, we envisioned the use of **90** as a unique, bifunctional phase transfer catalyst. As a PTC catalyst **90** introduces protonated DACs as compatible hydrogen bond donors, and also replaces the standard, localized, quaternary ammonium (or occasionally phosphonium) cation as the phase transfer functionality with two highly diffuse cyclopropenyl-based cations. The functional utility of **90** in phase transfer catalysis was projected to further benefit from: (1) a distinct partitioning of lipophilic and hydrophilic regions, (2) a π-polarizable naphthyl ring that would allow for π-π interactions (soft acid), (3) a highly charged dication electrostatic binding region (hard acid) that would facilitate the transport of anions into a lipophilic organic phase, and, (4) an H-bonding region engaging in both electrostatic and charge-transfer H-bond mediated molecular recognition (Figure 27). As

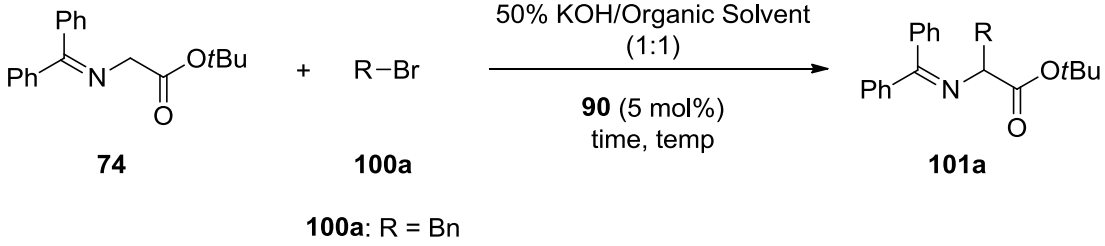
a corollary, it was foreseen that **89** or its monoprotonated derivate, **91**, might serve a further role, acting as an organic base to facilitate the deprotonation of pro-nucleophiles, thus providing another mechanistic dimension to phase transfer catalysis.

We chose to explore the potential of **90** as a PTC in the well-established alkylation of O'Donnell's glycine imine.[110] Initially there was uncertainty as to whether or not if **90** would undergo *N*-alkylation, as it would presumably be in equilibrium with **89** under basic conditions, or if steric encumbrance would impede alkylation. To investigate this possibility, 100 mg of **90** was mixed with excess benzyl bromide in a 1:1 mixture of DCM and 50% aqueous KOH, and the mixture was stirred at room temperature for eight hours. There was no evidence of the alkylated catalyst, and the catalyst could be easily recovered in near quantitative yield. Although there was no evidence of catalyst alkylation, it was shown that deprotonation under the reaction conditions did indeed occur, as established by dissolution of **90** in a 50% solution of KOH in D_2O at room temperature. In terms of catalyst stability, it is notable that when a sample of **90** was left in an aqueous 50% KOH solution at ambient temperature there was no noticeable decomposition after two weeks, as determined by ^{1}H NMR.

Given this encouraging preliminary result of catalyst stability, reaction conditions were screened for the alkylation of benzophenone imine **74** with benzyl bromide **100** (Table 5). The polar aprotic solvent acetonitrile (MeCN) resulted in complete consumption of the starting material in only 20 minutes at room temperature and a 92% of 101a. Comparatively, the use of slightly less polar dichloromethane (DCM) provided a similar outcome to that of MeCN, with full consumption of the starting material occurring in 45 minutes at room temperature to give 101a in 4% yield. The use of toluene

resulted in a slight background rate (*i.e*, product yield in the absence of catalyst **90**), extended reactions times, and poor overall product yield.

Table 5. Optimization of Phase Transfer Reaction Conditions with Catalyst **90**.



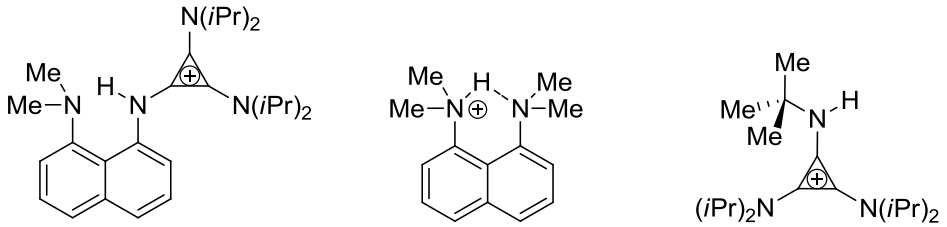
74 **100a** **101a**

100a: R = Bn

Entry	Solvent	Temp.	Time	Conversion[a]	Yield[b]
1	MeCN	25 °C	20 min	100%	92%
2	MeCN	0 °C	1 h	100%	91%
3	DCM	25 °C	45 min	100%	92%
4	DCM	0 °C	1.5 h	100%	89%
5	Toluene	25 °C	8 h[d]	51%[c]	36%[c]
6	Toluene	50 °C	8 h[d]	67%[c]	51%[c]

[a]Based on ^{1}H NMR spectroscopy. [b]Isolated yield after column chromatography. [c]In absence of catalyst **90** no conversion was observed except 6% for entry 6 based on ^{1}H NMR. [d]Noticeable background reaction (*i.e*, product formation in the absence of catalyst **90**) observed after 8 h.

To investigate the hypothesis that the lipophilic, bis-protonated, dicationic nature of **90** was critical for catalysis, three additional compounds, all sharing structural similarities with **90**, were employed as potential catalysts for the alkylation of **74** under the same reaction conditions (Figure 28). Namely, phase transfer alkylation of **74** was performed in the presence of 5 mol% of the hydrochloride salts of **95** (**102**) (the synthesis of which is shown in Section 2.4), Alder's Proton Sponge (**103**), and **72** (**104**). The use of **102** afforded only trace amounts of the benzylated product, while **103** resulted in no reaction, indicating that the protonated 1,8-diaminonaphthyl ring system was not the only structural feature of **90** leading to PTC catalysis. Reactions catalyzed by **104** gave only 9% of the desired product along with small amounts of alkylated by-product.[111] The failure of **102**, **103**, and **104** to impart any appreciable catalytic activity, despite their partial structural similarity to **90**, may suggest that **90** could be acting uniquely as a phase transfer catalyst.



102
trace product yield

103
No Reaction

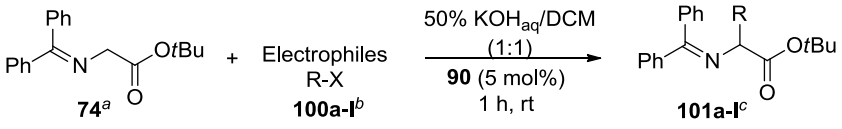
104
9 % product yield

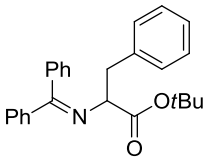
Figure 28. Alternative compounds screened as potential PTC catalysts of **74**.

The ability of **90** to function as a phase transfer catalyst was further explored using other electrophiles under the conditions applied for entry 3 in Table 5, although the corresponding reaction time was extended to one hour. The results are shown in Table 6. Naphthyl methyl bromide (**100b**) was comparable in reactivity to benzyl bromide,

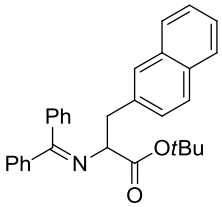
resulting in 92% isolated yield, while the sterically hindered secondary bromide **100c** afforded **101c** in 92% yield, demonstrating that substitution at the benzylic carbon was tolerated under the reaction conditions. The use of less reactive benzyl chloride (**100d**) and 4-methoxybenzyl chloride (**100e**) led to lower product yields, providing **101d** and **101e** in 60% and 54%, respectively. In contrast, 4-methyl benzyl bromide (**100e**) afforded a comparable yield to benzyl bromide with **101e** being isolated in 92% yield. The use of resonance-donating, electron-withdrawing 4-chloro substituted and strongly electron-withdrawing 4-nitro substituted benzyl bromides **100f** and **100g** also provided high product yields. Based on these trends, it would appear that the enhanced leaving group ability of a bromide relative to that of a chloride in benzyl halides effectively supersedes subtle electronic perturbations on reactivity introduced by the inclusion of a *p*-substituent. The aliphatic chain containing substrate (**100i**), proved to be a far less reactive electrophile, yielding only 10% of the desired product **101i**, though up to 90% yield could be obtained by increasing the reaction time to 48 hours. Lastly, allyl bromide (**100j**), allyl chloride (**100k**), crotyl bromide (**100l**), and cinnamyl bromide (**100m**) were all equally reactive and provided excellent yields. The regiochemical outcome with **100l** and **100m** indicated that a S_N2'-displacement of the bromide was not a competing process.

Table 6. Electrophile screen for the alkylation of **74**.

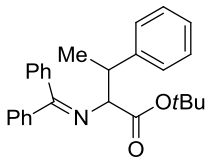




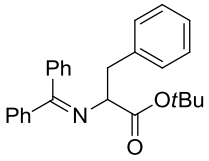
101a[d]
(91%)



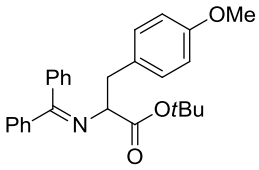
101b[e]
(92%)



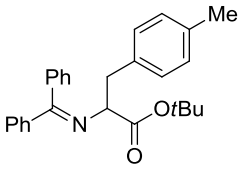
101c[f]
(91%)



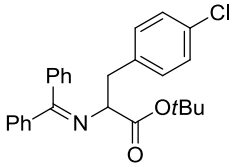
101d[g]
(60%)



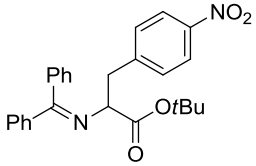
101e[h]
(54%)



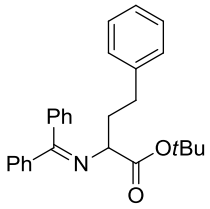
101f[i]
(92%)



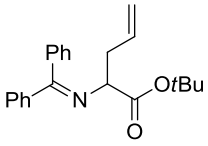
101g[j]
(93%)



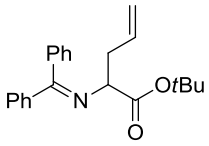
101h[k]
(92%)



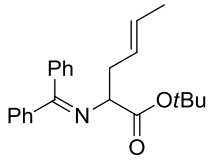
101i[l]
(10%)



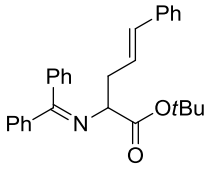
101j[m]
(92%)



101k[n]
(91%)



101l[o]
(91%)

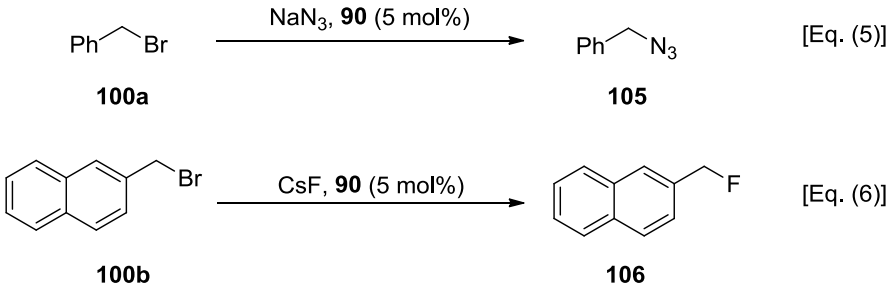


101m[p]
(90%)

[a]1 equiv. was used [b]1.2 equiv. were used [c] Yields based on isolated product obtained after column chromatography. No product was formed in any reaction in the absence of catalyst **90**. [d]**100a** = benzyl bromide. [e]**100b** = 2-(bromomethyl)naphthalene. [f]**100c** = (1-bromoethyl)benzene. [g]**100d** = benzyl chloride. [h]**100e** = 1-(bromomethyl)-4-methoxybenzene. [i]**100f** = 1-(bromomethyl)-4-methylbenzene. [j]**100g** = 1-(bromomethyl)-4-chlorobenzene. [k]**100h** = 1-(bromomethyl)-4-nitrobenzene. [l]**100i** = (3-bromopropyl)benzene. [m]**100j** = allyl bromide. [n]**100k** = allyl chloride. [o]**100l** = crotyl bromide. [p]**100m** = (*E*)-(3-bromoprop-1-en-1-yl)benzene.

Having demonstrated that **90** was a competent catalyst for interfacial PTC, we next applied it to nucleophilic fluoride and azide substitution reactions (Scheme 18), which are PTC processes generally believed to occur by extraction based mechanisms.[112] Emerging from these studies was the instructive finding that in stark contrast to the ability of **90** to facilitate interfacial PTC, it was a markedly less effective catalyst for extraction PTC. Even under a brief attempt at optimization, **90** provided only marginal rate acceleration in the benzylic fluorination of **100b** with CsF in MeCN with respect to the non-catalyzed background (Entry 7, Scheme 18). Furthermore, **90** had no effect on catalyzing the bromide displacement in **101a** by azide under PTC conditions (Entries 9-14, Scheme 18). One possible explanation for the lack of reactivity in these reactions is the absence of a suitable hydrogen bond acceptor on the electrophile, thus limiting the activity of **90** to a monofunctional phase transfer catalyst.

Scheme 18. Extraction-type PTC reactions.



Entry	Solvent	Nu	Temp.	Time	Yield	Control
1	Toluene	CsF	r.t.	24 h	12 %	N. R.
2	Toluene	CsF	reflux	24 h	28 %	11 %
3	DCM	CsF	r.t.	24 h	14 %	Trace
4	MeCN	CsF	r.t.	16 h	3 %	Trace
5	MeCN	CsF	60 °C	14 h	68 %	32 %
6	MeCN	CsF	Reflux	5 h	17 %	6 %
7	MeCN	CsF	Reflux	14 h	86 %	58 %
8	MeCN	KF	Reflux	24 h	4 %	N. R.
9	MeCN	NaN_3	r.t.	24 h	N.R.	N.R.
10	MeCN	NaN_3	80 °C	24 h	N.R.	N.R.
11	H_2O/DCM	NaN_3	r.t.	24 h	N.R.	N.R.
12	H_2O/MeCN	NaN_3	r.t.	24 h	N.R.	N.R.
13	H_2O	NaN_3	r.t.	24 h	N.R.	N.R.
14	H_2O	NaN_3	80 °C	24 h	N.R.	N.R.

While PTC reactions are known for being dynamic processes, wherein product formation is oftentimes complicated by "off-cycle" pre-equilibria, there is little doubt that the alkylation of O'Donnell's imine in this work proceeds by way of an interfacial hydroxide-initiated mechanism. Granted this fact, the more relevant question relates to the underlying source of the high catalytic activity of **90**. In part, it is thought to derive from the tendency of the catalyst to concentrate at the interfacial space, which is known

to be an important factor in hydroxide-initiated PTC reactions.[113] The innate organophilicity of **90** is also believed to play a critical role in enhancing the transport rate of anions from the interfacial phase to the organic layer, leading to faster reactions.[114] Though conjectural, a third aspect of **90** mediated PTC is the likelihood that the catalyst stabilizes the benzophenone imine enolate (**74**$^-$) via a set of heteronuclear positive charge assisted hydrogen bonds ((+)CAHB).[115] Lastly, it is reasoned that the strong basicity of both **89** and the aqueous layer would result in rapid deprotonation/re-protonation of **89** at the organic/aqueous interface. This would in turn toggle the solubility characteristics of the catalyst between that of a charged hydrophilic **90** dication with H-bonding residues to that of more lipophilic **89** or **91** species which would be prone to reside in the organic layer. In essence, a scenario would be established where the catalyst would be held at the interface by rapid protonation/deprotonation processes.

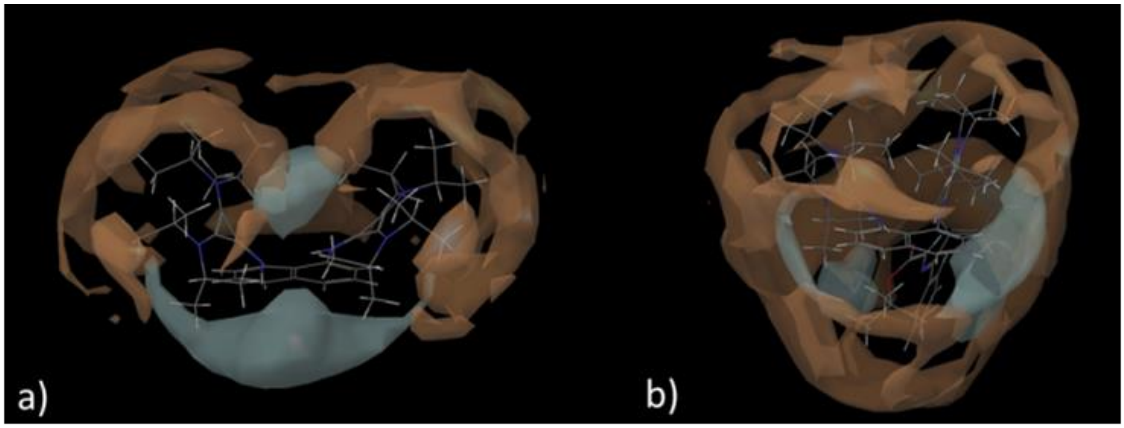
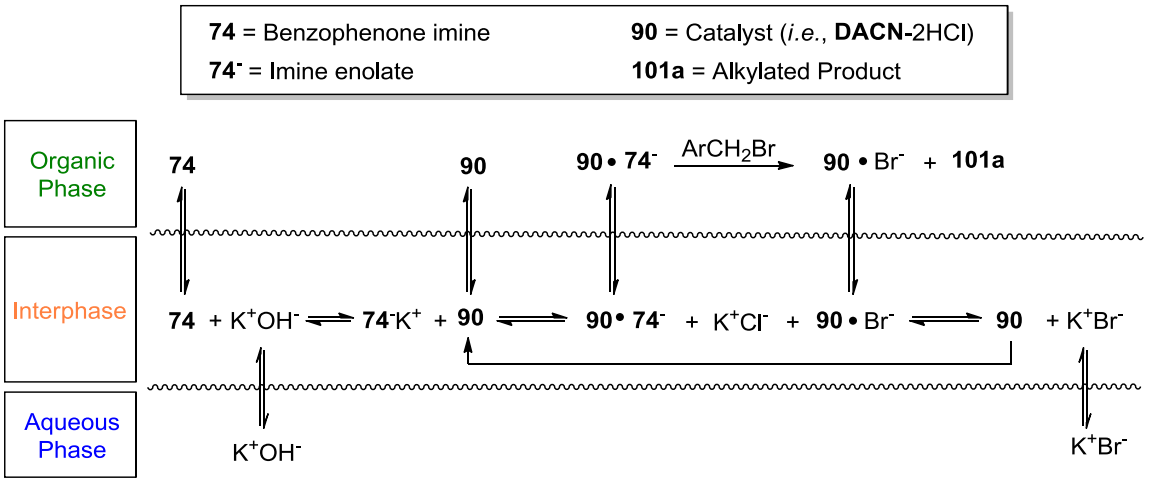


Figure 29. Hydrophobic (orange)/hydrophilic (blue) surfaces of **90** (left), and the **90•74**$^-$ complex (right), generated using Macromodel.

Modeling of the hydrophobic/hydrophilic surface areas of **90** and the corresponding hydrogen bound complex **90•74**$^-$ supported this conjecture as revealed by the hydrophobic/hydrophilic surface area plots depicted in Figure 29. Apparent from these plots was a distinct amphipathic division of hydrophobic/hydrophilic surfaces in **90** that suggested it would be prone to accumulate at organic/aqueous interfaces (Figure 29a). The hydrophilic surface density of **90•74**$^-$ was localized at the *re* and *si* faces of the enolate ester carbon and the hydrophilic surface was buried within the interior of this complex (Figure 29b). This structural arrangement should prolong the lifetime of the enolate in the organic phase and thereby increasing the probability of reaction with the electrophile.

Scheme 19. Proposed hydroxide-initiated interfacial PTC mechanism for alkylation of imine **100a** to afford **101a**.



As for the PTC cycle of these alkylation reactions, it is envisioned that a series of pre-equilibrium steps generates an effective concentration of a reactive benzophenone imine enolate **90•74**$^-$ complex in the interphase (Scheme 19). A preliminary model

derived from DFT calculations suggests the computed 34.9 kcal/mol binding affinity for this complex was driven by the formation of a bifurcated ((+)CAHB) H-bond/Columbic interaction (Figure 30). Migrating into the bulk of the organic phase **90•74**$^-$ then engages in C–C bond formation via a transition state assembly such as **TS1** (Figure 31) with an activation barrier of 10.7 kcal/mol (2.2 kcal/mol lower than that of the uncatalyzed transition state, see DFT computed geometries and thermochemical data) and elongated 2.46 Å C–C bond forming distance, which is suggestive of an early transition state, leading to alkylated product **101a**. The decrease in activation barrier in the presence of **90** is believed be a primarily result of counterion stabilization. Within the computed transition state the bromide leaving group is stabilized by H-bonding interactions with three isopropyl C-H's and a naphthalene C-H. In addition, the negatively charged bromide ion resides above the centroid of the positively charged cyclopropenimine ring.

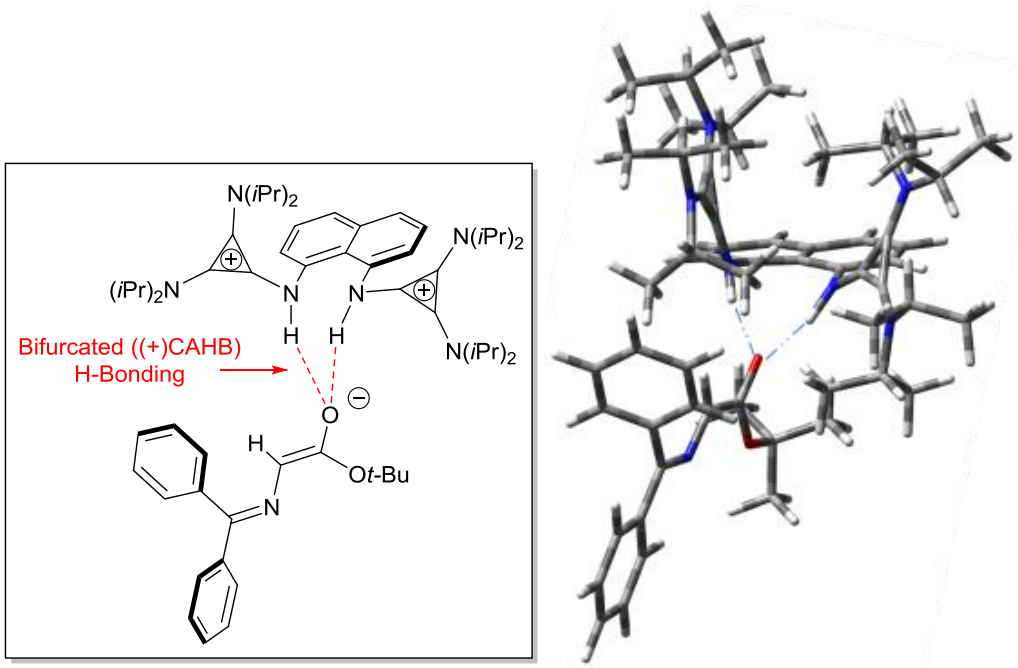


Figure 30. Chemdraw rendering of favorable binding interaction in **90•74**$^-$ (left). wb97xd/6-31G(d)/def2sv (solvent = dichloromethane) Computed complex **90•74**$^-$ (right).

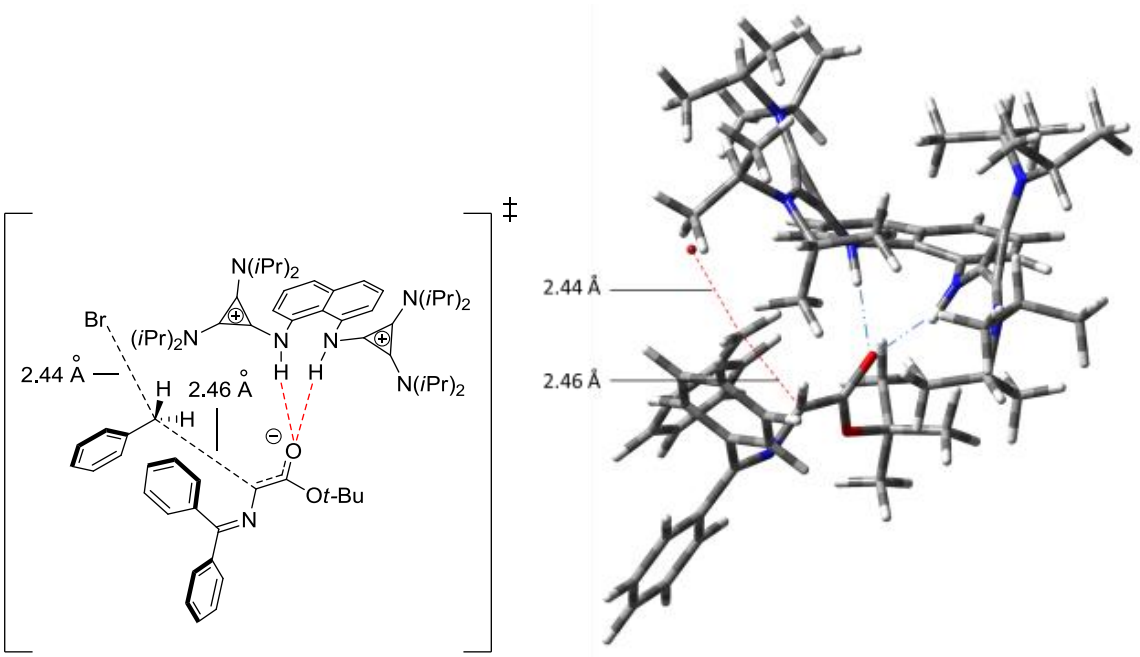


Figure 31. Chemdraw rendering of computed benzylation transition state, **TS1** (left). wb97xd/6-31G(d)/def2sv (solvent = dichloromethane) computed transition state **TS1** for alkylation (right).

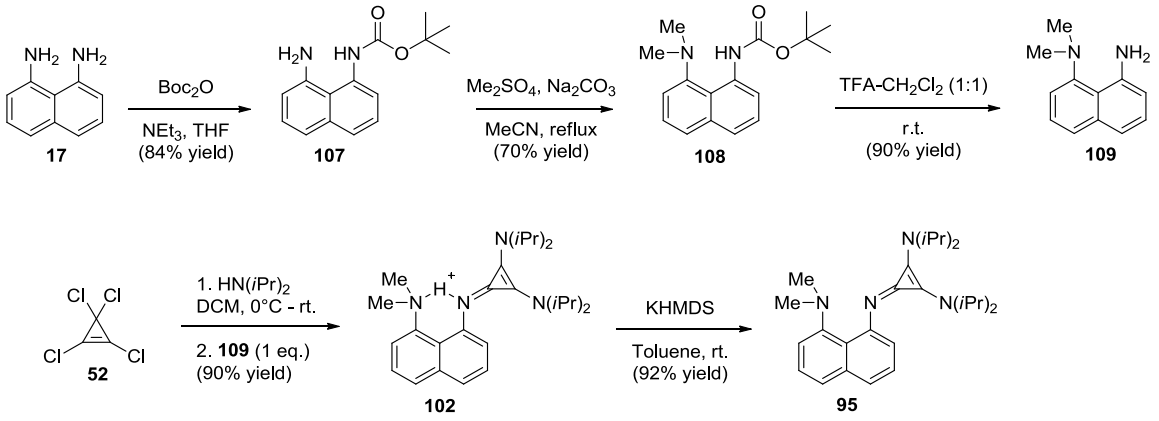
In summary, the bis-protonated salt of DACN was shown to be an effective catalyst for hydroxide-initiated interfacial PTC alkylations, while it was a poor catalyst for PTC processes occurring by extraction based mechanisms. The mechanistic role of **90** in the hydroxide-initiated interfacial PTC alkylations was investigated and is consistent with its role as a bifunctional, hydrogen bonding, phase transfer catalyst.

2.4 - The 'Janus' Sponge

Given the inability to isolate and characterize a monoprotonated derivative of **89** (*i.e.*, **91**), we sought to synthesize a derivative of **89** that might be more prone to monoprotonation. The envisioned derivative was a non-symmetric DAC-susbtituted proton sponge derivative akin to DACN (**90**) and Alder's archetypical sponge (**5**). Non-symmetric proton sponges are underrepresented, despite their considerable potential to

foster unique conceptual understanding and open innovative inroads to chemical advancement.[116] The target non-symmetric proton sponge derivative **95** (Scheme 20) possesses 1,8-naphthlyl substituted $N_{(sp2)}$ and $N_{(sp3)}$ hybridized nitrogens, and is comprised on the one hand from the prototypical DMAN sponge (**5**), and on the other, the DACN sponge (**90**), and is thus fittingly coined the "Janus" sponge.[117] Not only would this non-symmetric sponge provide us with information relating to how protonated DACs interact with sp^3 nitrogen centres, but it was envisioned that it might be amenable to isolation as a mono-protonated adduct and allow for an accurate experimental determination of its pK_a. The synthetic route to **95** allows for the synthesis of various other non-symmetric proton sponges having unique properties. Lastly, this report re-visits the internal charge transfer-based fluorescence associated with DMAN (**5**), in the context of a non-symmetric variant.

Scheme 20. Synthesis of Janus sponge **95.**



The synthesis of **95** (Scheme 20) began from commercially available 1,8-diaminonaphthalene, **17**, which was selectively mono-protected to afford **107** using the procedure of MacLachlan et al.[118] Methylation of the free nitrogen to afford **108** was performed with dimethyl sulfate. Optimal yields were obtained only on scales at or below

100 mg of **107**, with noticeable loss of product yield at larger scales. Methylation using MeI afforded lower yields. Subsequent trifluoroacetic acid (TFA) mediated *N*-Boc deprotection then afforded **109** in 90% yield (53% yield over the three steps). The dialkylaminocyclopropenyl group was then installed by drop-wise addition of diisopropylamine to a DCM solution of tetrachlorocyclopropene (**52**) at 0 °C, followed by drop-wise addition of a solution of **109** in DCM. The resulting reaction mixture was stirred for 18 h to provide salt **102** in 90% yield after chromatographic purification. Freebase **95** was then obtained in 92% yield (44% overall yield for 5 steps) using 0.5M KHMDS in toluene or alternatively NaH in THF.

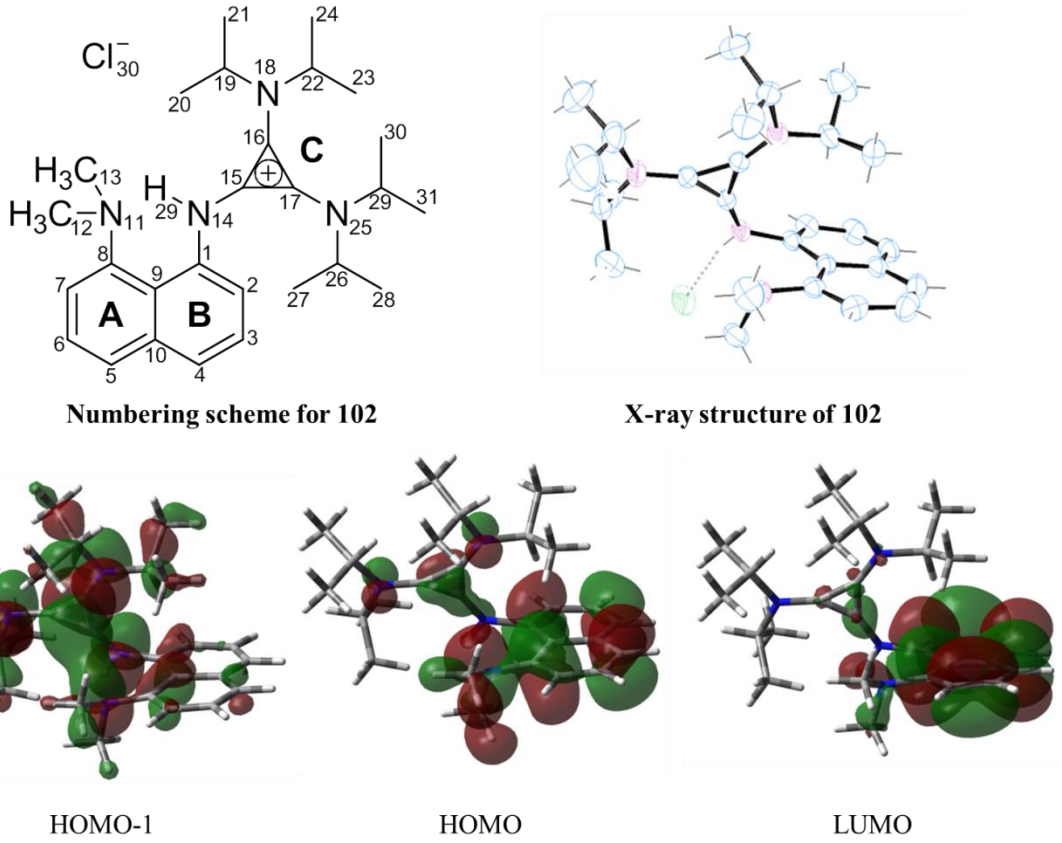


Figure 32. X-ray structure, numbering scheme, and selected B3LYP/6-31G(d,p) computed MOs for **102**$_{xray}$.

Remarkably, unlike its counterpart DACN (**89**), the non-symmetric sponge **95** was not susceptible to di-protonation in the presence of moderately strong acids such as acetic acid or concentrated HCl.

X-ray quality crystals of the hydrochloride salt of **95** (**102_{xray}**) were then obtained by vapor diffusion crystallization from benzene/EtOAc. Compound **102** was dissolved in a vial using slightly more than minimal amount of benzene required for dissolution. The vial was then placed in a beaker filled half an inch deep with ethyl acetate. The beaker was then capped with aluminum foil and placed in a 5 °C fridge, unperturbed for 72 hours. The corresponding molecular structure determined by single-crystal X-ray diffraction analysis is shown in Figure 32. The structure of **102_{xray}** is striking for several reasons. First, in keeping with the X-ray structure of **90**, the typical N(11)···H(29)-N(14) IHB observed in most proton sponges is absent, having been superseded by a N(14)H(29)···Cl(30) hydrogen—halogen bond (2.29 Å). Furthermore, the relatively long N(11)···N(14) interatomic distance (2.81 Å) and noticeable distortion of the naphthalene backbone ($\theta_{5\text{-}10\text{-}9\text{-}1}$ = 175.4°) are more consistent with that of neutral proton sponges. Another feature is the hybridization of N(14), which displays significant sp^3 character, and the presence of a lone pair, as supported by NBO calculations. This feature is presumably linked to the two amino groups adopting an *in-out* configuration, where the N(11) electron pair is pointed in towards N(14), but the electron pair of N(14) is directed outwards from the naphthalene ring. Though this type of geometry is not without precedence,[119] to the best of our knowledge it represents the first reported isolation of a proton sponge with an *in-out* configuration lacking an *ortho*-substituent, and the first instance of this type of configuration in a protonated proton sponge. The

cyclopropenimine ring (ring C) is oriented overtop of the naphthalene backbone (ring A/B), opposite to what has been observed in previously reported proton sponges having basic sp^2 nitrogens, including **89**.[120]

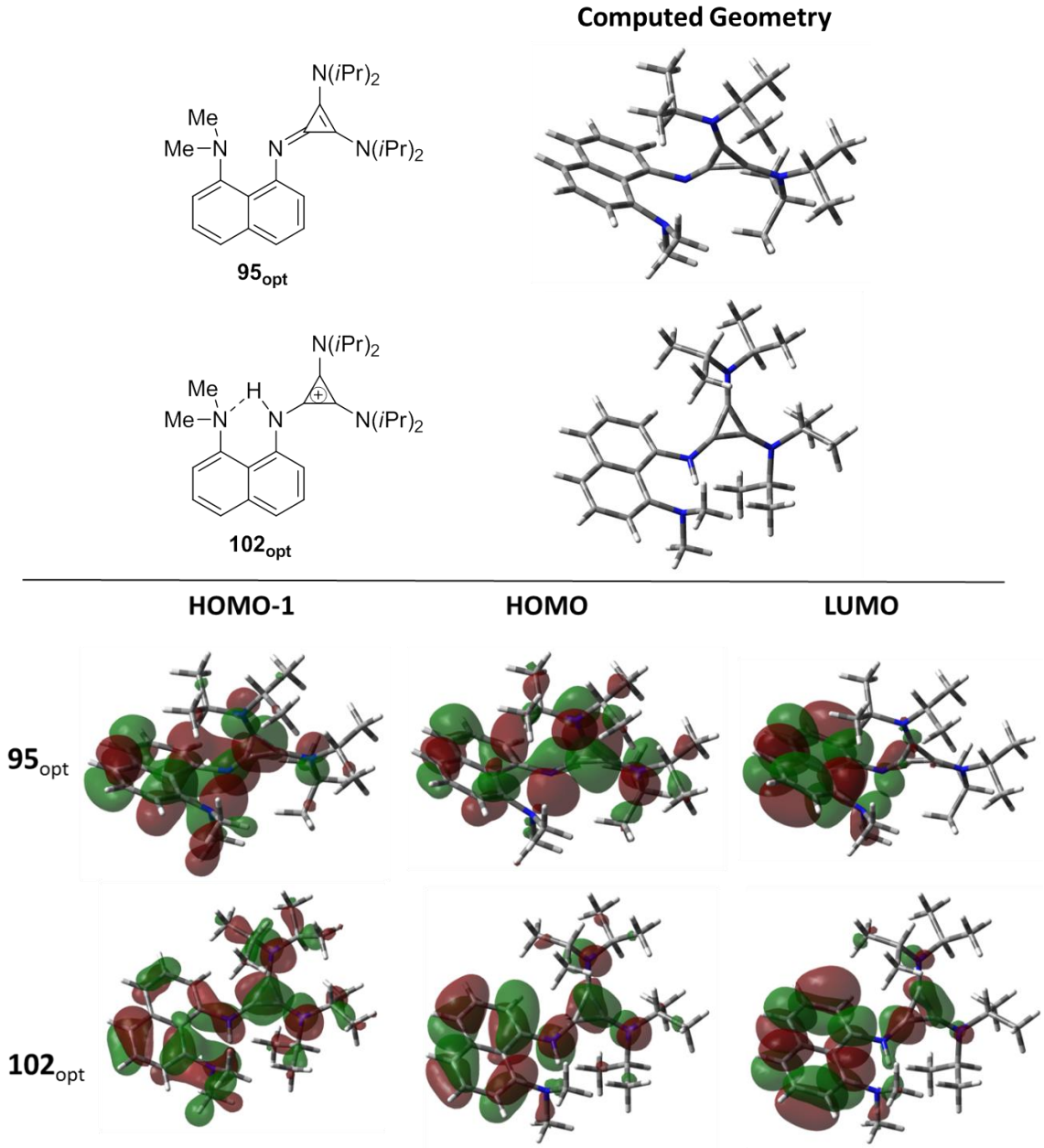


Figure 33. B3LYP/6-31G(d,p) optimized geometries and selected MOs for compounds **95$_{opt}$** and **102$_{opt}$**.

While all of the factors responsible for this unprecedented geometry are unknown, one contributing element is a stabilizing donor-acceptor interaction between the N(11)-lone pair and the cyclopropenyl π-system (N(11)···C(15) = 2.84 Å), as revealed NBO analysis ($N(11)_{LP} \rightarrow C(15)_{\sigma^*}$ E_{NBO} = 3.1 kcal/mol), and the computed MOs of **102$_{xray}$** (Figure 33, HOMO-1). In contrast to the X-ray crystal structure, the DFT B3LYP/6-31G(d,p) optimized geometry of **102** (**102$_{opt}$**, Figure 33), but lacking a chloride ion, did possess a N(11)···H(29)-N(14) intramolecular hydrogen bond (1.77 Å). The geometry obtained when optimized in the presence of the Cl^- counterion matched the crystal structure quite closely, leading us to believe that the observed molecular geometry is not simply an effect of crystal packing forces. A detailed inspection of computed **102$_{opt}$** proved instructive as both the aromatic naphthalene backbone ($\theta_{5\text{-}10\text{-}9\text{-}1}$ = 178.3°) was found to be less distorted and the N(11)···N(14) interatomic distance of 2.68Å significantly shorter than in **102$_{xray}$**, due to presence of a highly non-symmetric IHB having a N(14)—H(29) bond distance of 1.05 Å and N(11)···H(29) H-bonding contact measuring 1.77 Å. The *in-in* electron pair configuration in **102** allowed for effective delocalization of the N(14) lone pair into the naphthalene ring system, resulting in ring C being tilted away from the naphthalene backbone and providing a geometry that was more in line with that of conventional proton sponges. The computed geometry of freebase **95** (**95$_{opt}$**) shown in Figure 33 closely resembled that of **102$_{xray}$**, more so than does **102$_{opt}$**. Observed in **95$_{opt}$** was substantial distortion of the naphthalene backbone from ideal planarity ($\theta_{5\text{-}10\text{-}9\text{-}1}$ = 171.4°), along with elongation of the N(11)···N(14) interatomic distance to 2.91 Å. Meanwhile, the calculated N(14)—C(1) bond distance of 1.40 Å was slightly shorter than the N(11)—C(8) bond distance (1.42 Å), yet longer than the N(14)—C(15) bond distance

(1.32 Å). Like **102$_{xray}$**, **95$_{opt}$** displayed an *in-out* type geometry with ring C tilted towards the A/B ring system and as such it would appear the Janus sponge, regardless of whether or not it is protonated, favors an *in-out* lone pair-lone pair geometry with the cyclopropenyl ring geared inwards towards the naphthalene ring. Thus it would clearly seem the observed molecular structure of **102** is not simply a result of a strong N(14)H(29)···Cl(30) hydrogen-halogen bond, but instead originates from the aforementioned stabilizing donor-acceptor interaction between the N(11) lone pair and the cyclopropenyl π–system. Shown in Figure 33 are the corresponding HOMO-1, HOMO, and LUMO of **95$_{opt}$** and **102$_{opt}$**. In both cases the HOMO possesses significant orbital density on the cyclopropenyl ring which is consistent with previous reports detailing the electron rich nature of the cyclopropenyl cation,[121] as well as those reports of further oxidizing the cyclopropenyl cation to the radical dication.[122] In this respect, there was minimal contribution from the N(11) lone pair in the HOMO of **102$_{opt}$** or **95$_{opt}$**, as evidenced by the lack of orbital density. In terms of the HOMO-1, **102$_{opt}$** displays substantial orbital contribution from the N(11) lone pair and the cyclopropenyl ring system, which is perhaps not surprising considering the similar geometry to **102$_{xray}$**. Nevertheless, even though **95$_{opt}$** also displayed significant contribution from the N(11) lone pair and cyclopropenyl ring system to the HOMO-1, the lobes are not oriented towards one another, nor are they of the same sign, in contrast to **95$_{opt}$**. Lastly, both LUMOs are primarily on the naphthalene backbone, with a small contribution from the cyclopropenyl ring system in **102$_{opt}$**.

Table 7. B3LYP/6-311++G(d,p)//B3LYP/6-31G(d,p) calculated NICS(-1),NICS(0), and NICS(1) values for **95, 102_{opt},** and **102_{xray}.**

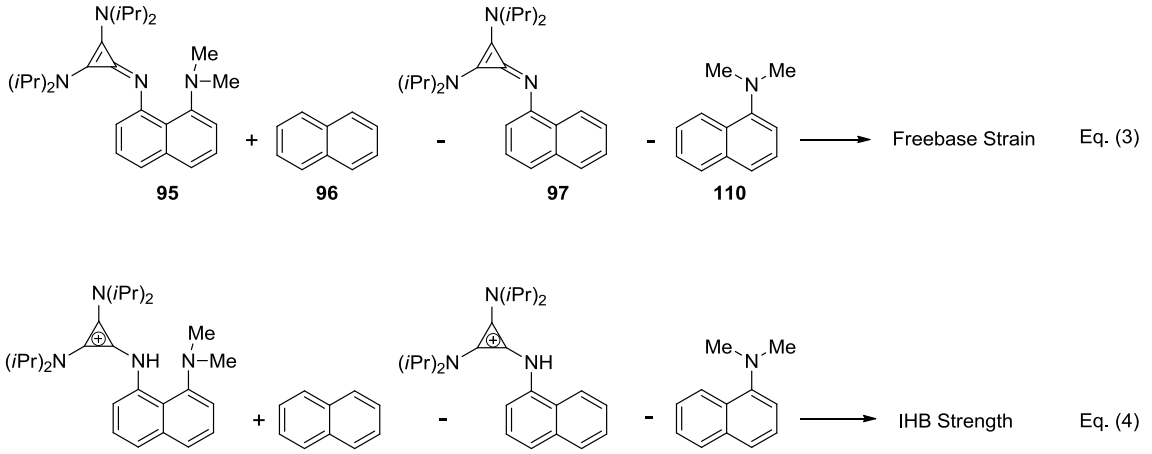
		95_{opt}	**102_{opt}**	**102_{xray}**
Ring A	NICS(-1)	9.22	10.80	10.46
	NICS(0)	8.11	9.39	8.76
	NICS(1)	9.43	10.31	10.01
Ring B	NICS(-1)	9.28	10.15	9.97
	NICS(0)	8.34	8.76	8.97
	NICS(1)	10.13	9.57	10.56
Ring C	NICS(-1)	8.72	8.78	9.22
	NICS(0)	29.84	31.08	32.20
	NICS(1)	8.46	8.96	9.08

To ascertain the respective aromaticity of the A, B, and C ring systems, Nucleus Independent Chemical Shift (NICS) calculations were performed on **95_{opt}**, **102_{opt}**, and **102_{xray}**, at the centre of each ring system (NICS (0)), as well as 1 Å above (NICS (1)) and 1 Å below (NICS (-1)) the centre of each ring to circumvent σ–contamination from the carbon framework of the ring, which is particularly prominent within the small cyclopropenyl ring systems. As seen from Table 7, with the exception of the NICS(1) values for Ring B, there is an increase in the NICS values for all three ring systems upon protonation of N(14), regardless of the geometry. For **102_{opt}** the increase in NICS values for rings A and B may be a result of the IHB, as the N(11) lone pair is oriented orthogonal to the naphthalene ring, substantially diminishing perturbation of the aromatic backbone. However, in the case of **102_{xray}**, there is no IHB, and the increase in aromaticity of the A/B ring system is likely a consequence of N(11) lone pair donation into ring C, rather than ring A. Not surprisingly, an increase in the C ring NICS values occurred for both **102_{xray}** and **102_{opt}**, presumably as a direct result of generating the cyclopropenyl cation upon protonation. The larger NICS values obtained for ring C in

102$_{xray}$ relative to **102$_{opt}$** conceivably originate from N(11) lone pair donation into the cyclopropenyl cation, thus suggesting the geometry of **102$_{xray}$** is more conducive to cyclopropenyl cation stabilization.

The PA of **95** was computed at the B3LYP/6-311G++(d,p)//B3LYP/6-31G(d) level taking into account thermal corrections estimated at the B3LYP/6-31G(d) level. A computed gas phase basicity of 266.8 kcal/mol was found, which was substantially less than that of DACN (282.3 kcal/mol) computed at the same level of theory. A relative pK_a (MeCN) calculation at the IEFPCM/B3LYP/6-311G++(d,p)//B3LYP/6-31G(d,p) level, using TMNG as a reference base (see Appendix B), estimated the pK_a value at 23.9 in MeCN. To substantiate these computational results, the pK_a of **95** was experimentally measured in MeCN using a previously reported NMR titration approach[53a] (see Appendix B). Gratifyingly, using tetramethyl guanidine (TMG) as a reference base, the measured pK_a value of 23.8 was very close to the computed value.[123] The lower pK_a of **95**, relative to *t*-Bu-(bisdiisopropylamino)cyclopropenimine, **72** (pK_a = 26.9[53a]), indicates that the withdrawing effect of the naphthalene ring decreases the basicity more than it is increased by the presence of freebase destabilization arising from the proton sponge backbone (see Figure 26)

Scheme 21. Homodesmotic reactions calculated at the B3LYP/6-31G(d,p) level to demonstrate the contribution of repulsive interactions in the neutral base (Eq. (3)), and the IHB strength (Eq. (4)) to the PA of **95**.



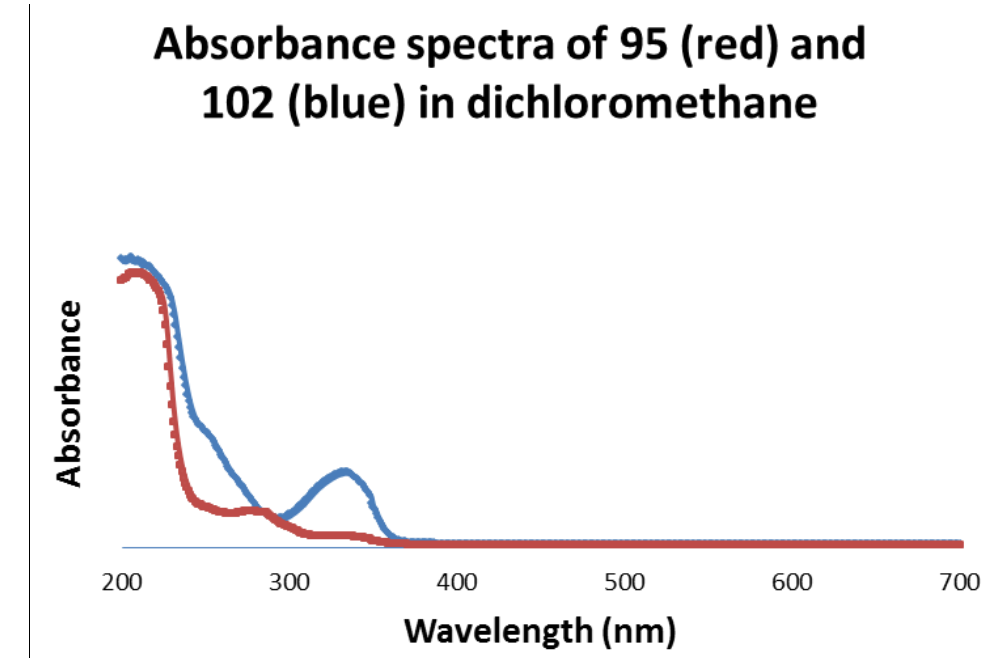
The homodesmotic reactions in Scheme 21 were applied to discern the effect of ground state stabilization (Equation (3)) and IHB strength (Equation (4)) on the basicity of **95**. According to Equation (3), ground state stabilization contributes 7.7 kcal/mol, while Equation (4) suggests that the stabilization associated with the IHB was found to be only 0.6 kcal/mol. Table 8 provides a useful comparison between **95** and **89**, and shows that the roughly one thousand fold difference in K_a originates predominantly from a decrease in the freebase strain. Though the hydrogen bond energy in **95** was only half that observed in **89**, its effect on the pK_a is likely not as significant. AIM analysis supported the existence of an IHB by presence of a bond critical point between N(11) and H(29) (See Appendix A), which was further probed by NBO analysis, revealing a donor-acceptor interaction energy of 26.0 kcal/mol from the N(11) lone pair into the N(14)—H(29) antibonding orbital. Given the lower ground state destabilization and relatively

weak IHB, it is perhaps not surprising that **95** possess a hydrogen bond to the chloride ion, rather than an IHB.

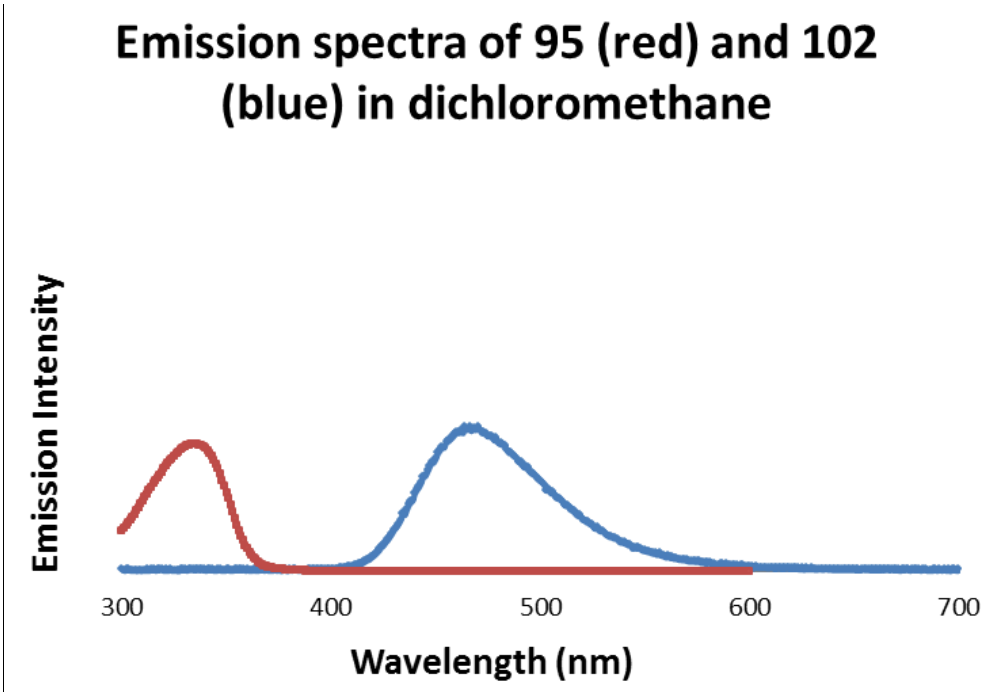
Table 8. Comparison between Janus and DACN.

	IHB E_{NBO} (kcal/mol)	IHB Strength (Eq. (3)) (kcal/mol)	Freebase Strain (Eq. (4)) (kcal/mol)	Computed PA (kcal/mol)	Calculated pK_a	Measured pK_a
95 (Janus)	26.0	0.6	7.7	266.8	23.9	23.8
89 (DACN)	27.3	1.2	21.1	282.3	27.0	--

One the most intriguing features of the Janus sponge, **95,** is its luminescent properties (Figure 34). Upon absorption of UV light ($\lambda_{max} = \lambda_{ex}$ = 283 nm) in a dichloromethane solution at room temperature, **95** emits UV light at a longer wavelength (λ_{em} = 341 nm), corresponding to a Stokes shift of 58 nm. Conversely, a dichloromethane solution of its protonated salt, **102**, absorbs light in the long range UV region ($\lambda_{max} = \lambda_{ex}$ = 333 nm) and emits light in the visible wavelength (λ_{em} = 472 nm), corresponding to a Stokes shift of 139 nm. This trend is opposite to that reported with DMAN (**5**) in acetonitrile, wherein the neutral species absorbs at a higher wavelength (λ_{max} = 340 nm) than the protonated species (**5**H^+, λ_{max} = 286 nm).[124] The change in Stokes shift and fluorescence intensity between **95** and **102** is substantial, though not all too surprising considering the generation of aromaticity upon protonation which constitutes a considerable geometric and electronic transformation.



a)



b)

Figure 34. (a) UV/Vis absorption spectra of **95** and **102** as $1x10^{-5}$ M solutions in dichloromethane. (b) Emission spectra of **95** and **102** as $1x10^{-5}$ M solutions in dichloromethane. Emission spectra taken at room temperature, with entrance and exit slit widths of 5 mm.

c)

Figure 35. (c) Visual portrayal of the luminescent character of compound **102** as a solid (left vial) and as a solution in dichloromethane (right vial).

Notably, under persistent illumination **102** displays excellent photostability (*i.e.*, its quantum yield does not decrease after prolonged exposure to light) as a solid and in solution (Figure 34c), having a quantum yield of 0.37 in ethanol (See Appendix C for details on quantum yield measurements).

There has been extensive study into the photophysical properties of DMAN (**5**), which may shed light on the possible fluorescent origins of **95**.[124,125] According to these reports, the electronic excitation of DMAN originates from its ^1L_a state, with considerable contribution from the NMe_2 groups, and after internal conversion leads to the emissive, naphthalene-based, $1\pi^*$ internal charge transfer (ICT) state. Twisting of the methyl groups on N(11) (i.e. geometry re-organization) plays a major role in the large Stokes shift. By analogy to this role of NMe_2 in the fluorescence of DMAN, the NMe_2 group of the Janus sponge is likely important for its luminescent character. Furthermore, there is little doubt that the aromatic cyclopropenium ion also plays a key role in the electronic

transition(s) leading to fluorescence, considering it is the only structural difference between **95** and DMAN. From these two conjectures, (that the NMe_2 group and cyclopropenium ion are key factors in Janus's luminescent character) and given that the computed LUMO of $\mathbf{102_{xray}}$ (or the LUMO+1 for that matter, see Appendix C) does not possess significant contribution from either the NMe_2 group or the cyclopropenium ion (see Figure 32), excitation likely originates from a MO involving both the cyclopropenyl cation and the NMe_2 group (*i.e.*, the HOMO or HOMO-1), while emitting from a MO involving the naphthalene system.

Though the exact electronic transitions leading to **102**'s fluorescent properties remain uncertain, the drastic effect observed upon adding a single cyclopropenimine unit is evidence that cyclopropenimine based fluorescent-probes, LEDs and dyes may be worth studying. This fluorescent nature of **102** expands the potential applications of cyclopropenimines, especially considering **102** represents a fluorescent compound derived from the protonation of a neutral, organic superbase, with the potential to be a bidentate metal chelating ligand.

In conclusion we have reported the synthesis and theoretical investigation of a non-symmetric, DAC functionalized proton sponge derivative, coined the 'Janus' sponge. The protonated cyclopropenimine unit displayed weak hydrogen bonding to the adjacent NMe_2 substituent, and was found to be superseded by a hydrogen—halogen bonding interaction to a Cl^- counterion. Associated with this fact was the rare *in-out* geometry of the basic nitrogens, which represents the first such instance in the absence of an *ortho*-substituent as well as in a protonated state. Furthermore, N_{LP} donation into the cyclopropenium cation was found to stabilize its unprecedented geometry. The pK_a of **95**

was measured to be 23.8, in good agreement with the computed value of 23.9. Lastly, **102** displayed vibrant luminescence both in solution and in the solid phase, representing the first example of a cyclopropenimine-based fluorescent organic compound.

2.5 - Investigating Fluorescence of DACs:

Over the past several decades, small fluorescent organic molecules have been used in numerous industrial applications such as light emitting diodes,[126,127,128] chemical sensors,[129,130] biological probes,[131] and cellular imaging agents.[132,133] We were interested in further studying the fluorescent nature of **102**. To this end, a series of derivatives were synthesized in order to establish structure-activity relationships and determine how each component of **102** affects its fluorescence. The corresponding set of derivatives that were synthesized for this purpose are shown in Figure 35, and include the known compounds **104** and **116**.

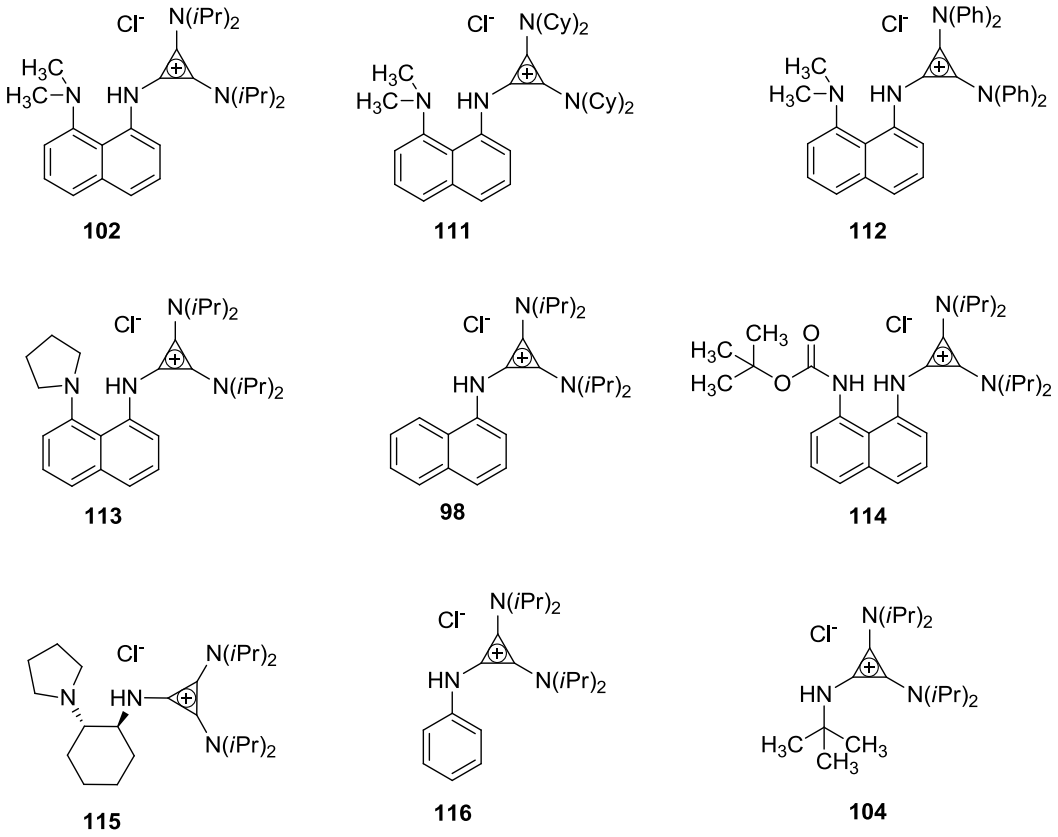
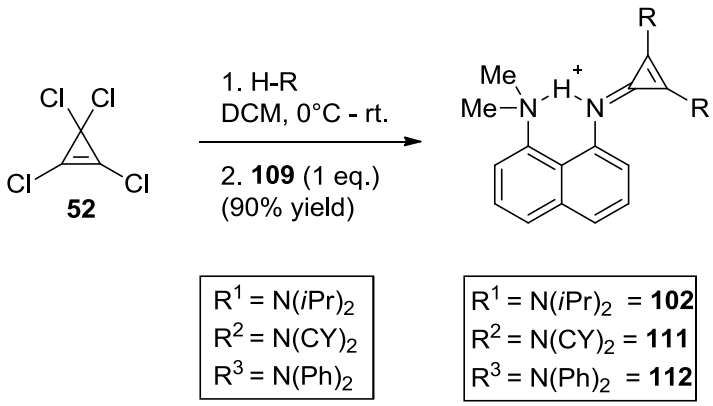


Figure 36. Selected set of cyclopropenimine derivatives.

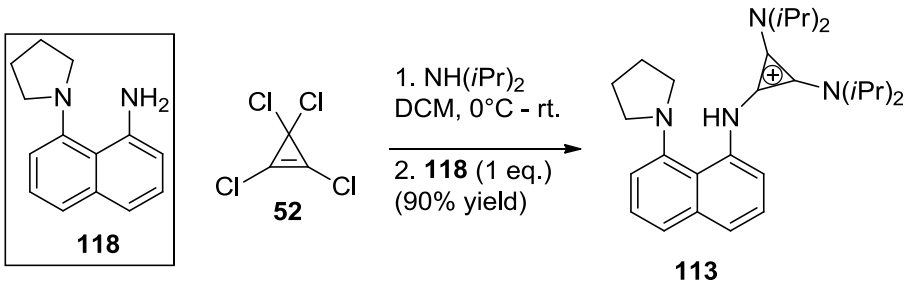
The synthesis of bis(dicyclohexylamino)cyclopropenimine derivative **111** and bis(diphenylamino)cyclopropenimine derivative **112** followed the same synthetic sequence implemented for the synthesis of **102** (Scheme 22), by substituting the secondary amine with either dicyclohexylamine or diphenylamine, respectively.

Scheme 22. Synthetic procedure for the synthesis of **95**, **111**, and **112**.



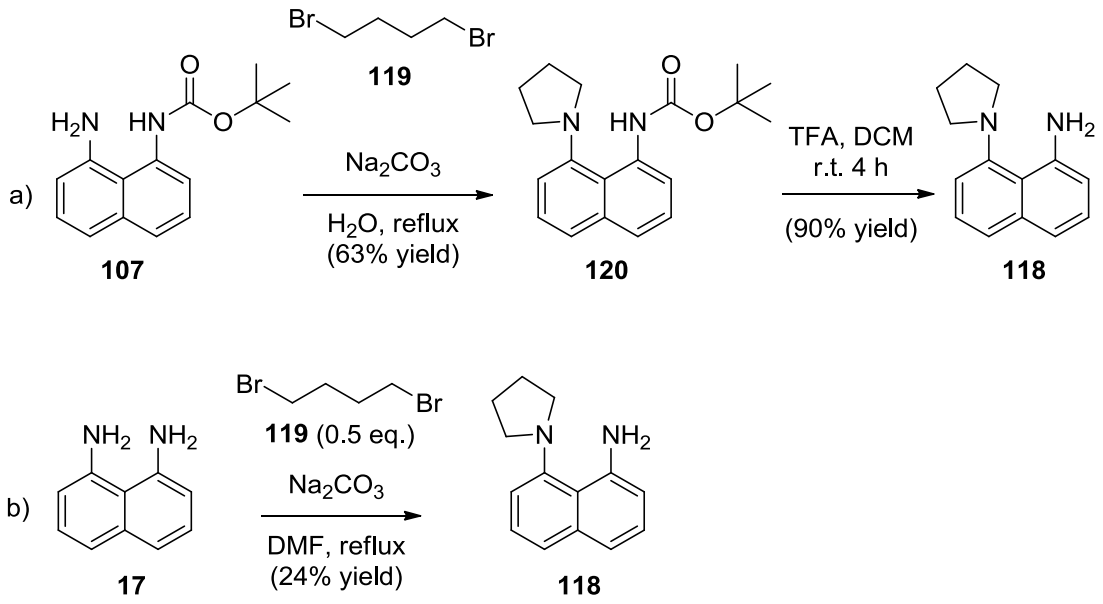
Derivative **113** was also synthesized using an similar route to that of **102**, whereby intermediate **118** was used in place of 1,8-diaminonaphthalene (Scheme 23).

Scheme 23. Synthetic procedure for the synthesis of **113**.



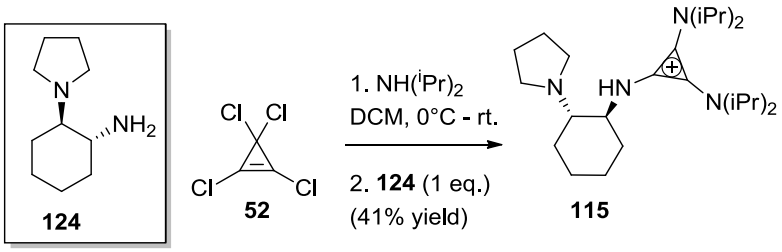
Intermediate **118** was synthesized using two different approaches, shown in Scheme 24a and 23b. A protection/deprotection sequence (Scheme 24a) was successful in producing **118** in 42% yield over three steps (the synthesis of **107** is a one-step procedure with 84% yield, as seen in Scheme 20).

Scheme 24. Two alternate synthetic procedures for the synthesis of **118**.



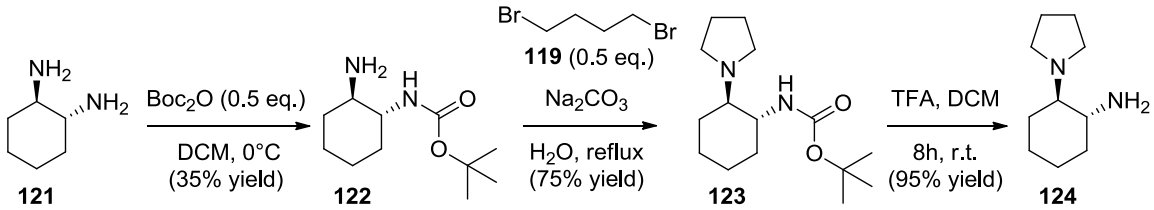
However, the protection/deprotection steps proved to be superfluous, as employing the methodology reported by Kovačević[134] afforded **118** in one step from **17** in 24% yield (Scheme 24b). Though this approach affords only slightly more than half of the yield obtained using method 23a, it eliminates two synthetic manipulations, in addition to eliminating the requisite crystallization of **107**, and purification of **120** by column chromatography. As such, the method outlined in Scheme 24b is likely superior based on the associated synthetic ease and cost efficiency. Derivative **114** was synthesized using the same route for the synthesis of **102** (Scheme 20), wherein intermediate **107** is used in place of **109** as the primary amine. Derivatives **98**, **116** (the hydrochloride salt of **94**), and **104** (the hydrochloride salt of **72**) were also synthesized according to Scheme 23 by employing 1-naphthylamine, aniline, and *tert*-butylamine, respectively in place of intermediate **118**. Lastly, the synthesis of derivative **115** (Scheme 25) is parallel to that of **113**, employing in part method 24a.

Scheme 25. Synthetic procedure for the synthesis of derivative **115**.



The synthesis of derivative **115** employed intermediate **124** as shown in Scheme 25. The synthesis of **124** followed a protection/deprotection sequence (Scheme 26), as the method of Kovačević proved unsuccessful for this substrate.

Scheme 26. Synthetic procedure for the synthesis of intermediate **124**.



Upon synthesis and characterization of the derivatives in Figure 35, the UV/Vis absorption and corresponding emission spectra were recorded in both dichloromethane and ethanol solvent (Table 9). The quantum yields were recorded in ethanol, relative to an anthracene standard (See Appendix C). For comparison, literature data from two additional compounds (**5**H^{+}[135] and **110**[136]) have been included. The derivatives in Figure 35 were divided into two separate groups; those derivatives with a molar attenuation coefficient greater than 1×10^3 (Group A = **102**, **111**, **112**, **113**, and **114**) and those with a molar attenuation coefficient less than 1×10^3, (Group B = **98**, **115**, **116**, and **104**).

Table 9. Summary of Group A absorbance maxima in DCM and EtOH (and MeCN for **102**), emittance maxima from excitation at 334 nm, quantum yield, and molar attenuation coefficients. * *Literature data used*.

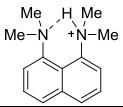
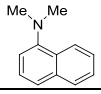
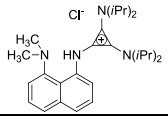
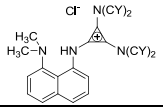
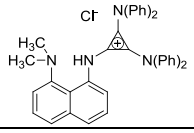
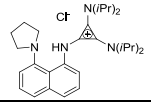
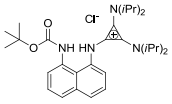
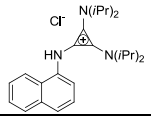
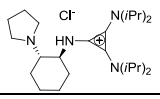
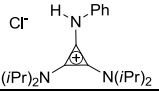
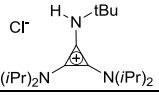
Compound	Absorbance λ_{max}	Emission λ_{em} (λ_{ex} = 334 nm)	Stokes Shift	Molar Attenuation Coefficient ($M^{-1}\,cm^{-1}$)	Quantum Yield
*5 H^+ 	MeCN: 286 nm	MeCN: 480 nm	MeCN:194 nm	--	0.004
*110 	MeCN: 312 nm	MeCN: 419 nm	MeCN:107 nm	4.47×10^3	0.17
102 	DCM: 333 nm EtOH: 334 nm MeCN: 334 nm	DCM: 471 nm EtOH: 472 nm MeCN: 486 nm	DCM: 138 nm EtOH: 138 nm MeCN:152 nm	4.70×10^3	0.37
111 	DCM: 334 nm EtOH: 335 nm	DCM: 471 nm EtOH: 476 nm	DCM: 137 nm EtOH: 141 nm	9.10×10^3	0.26
112 	DCM: 346 nm EtOH: 345 nm	DCM: 487 nm EtOH: 487 nm	DCM: 141 nm EtOH: 142 nm	1.66×10^4	0.18
113 	DCM: 333 nm EtOH: 333 nm	DCM: 469 nm EtOH: 476 nm	DCM: 136 nm EtOH: 143 nm	8.60×10^3	0.43
114 	DCM: 328/368 nm EtOH: 318/358 nm	DCM: 412/446 nm EtOH: 414/448 nm	DCM: 78 nm EtOH: 90 nm	6.24×10^3	0.33

Table 10 Summary of Group B absorbance maxima in DCM and EtOH, emittance maxima from excitation at 334 nm, quantum yield, and molar attenuation coefficients.

Compound	Absorbance λ_{max}	Emission λ_{em} (λ_{ex} = 334 nm)	Stokes Shift	Molar Attenuation Coefficient (M^{-1} cm^{-1})	Quantum Yield
98 	DCM: 326 nm EtOH: 320 nm	DCM: 459 nm EtOH: 448 nm	DCM: 133 nm EtOH: 129 nm	8.80×10^2	0.11
115 	DCM: 328 nm EtOH: 325 nm	DCM: 461 nm EtOH: 468 nm	DCM: 133 nm EtOH: 143 nm	5.00×10^2	0.05
116 	DCM: 338 nm EtOH: 322nm	DCM: 463 nm EtOH: 468 nm	DCM: 125 nm EtOH: 146 nm	2.70×10^2	0.11
104 	DCM: 326 nm EtOH: 322 nm	DCM: 462 nm EtOH: 468 nm	DCM: 136 nm EtOH: 146 nm	2.00×10^2	0.09

Several important pieces of information can be extracted from the datasets in Tables 9 and 10. First, each cyclopropenimine derivative possesses an absorbance maximum between 318 nm and 345 nm and a fluorescence emission maximum in the range of 414 nm and 487 nm. For comparison, in acetonitrile 1-dimethylaminonaphthalene has an absorbance maxima at 312 nm, and emission maxima at 419 nm, and protonated 1,8-bis(dimethylamino)naphthalene (**5**H^+) has an absorbance maxima at 286 nm and emission maxima at 480 nm. Accordingly, the absorbance/emittance profiles of the cyclopropenimine derivatives in Figure 35 resemble that of the protonated proton sponge (**5**H^+). However, the absence of an aminonaphthalene moiety in **115**, **116**, and **104** suggests that the cyclopropenimine core

itself coincidentally shares a similar spectroscopic profile. The absorbance profiles of Group A are shown in Figure 36. Notably, derivatives **102**, **111**, and **113** all have very similar absorbance profiles, while **112** is noticeably red-shifted and **114** is significantly blue-shifted. Additionally, **112** possesses a second absorption band with a maximum at 362 nm.

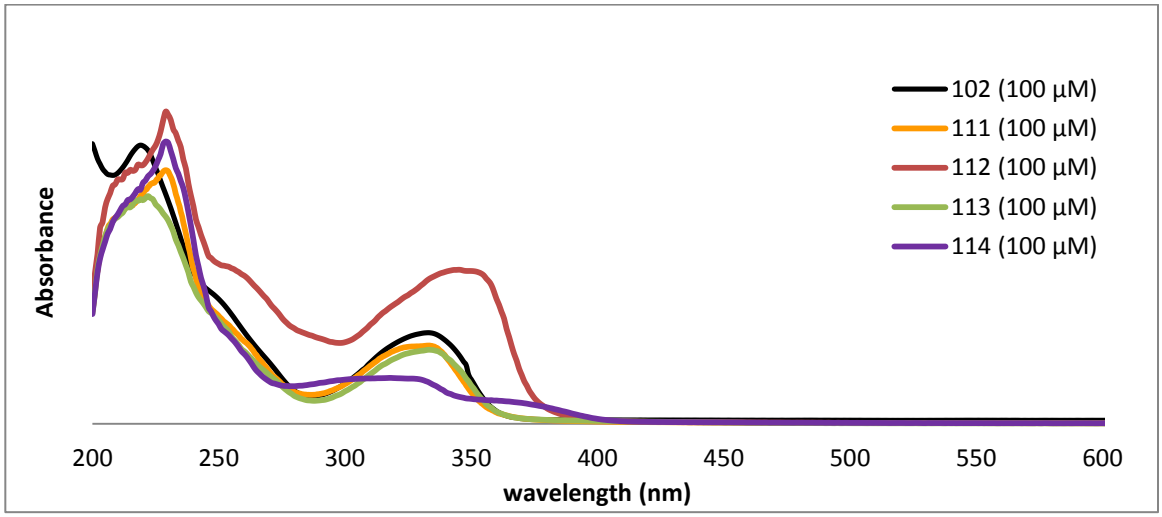


Figure 37. UV/Vis absorbance spectra recorded for Group A (**102**, **111**, **112**, **113**, and **114**) as 100 µM solutions in EtOH at ambient temperature.

The fluorescence emission spectra for Group A are shown in Figure 37. Derivatives **102**, **111**, and **113** share similar emission maxima (λ_{em} = 472 nm, 476 nm, and 476 nm, respectively, in EtOH).

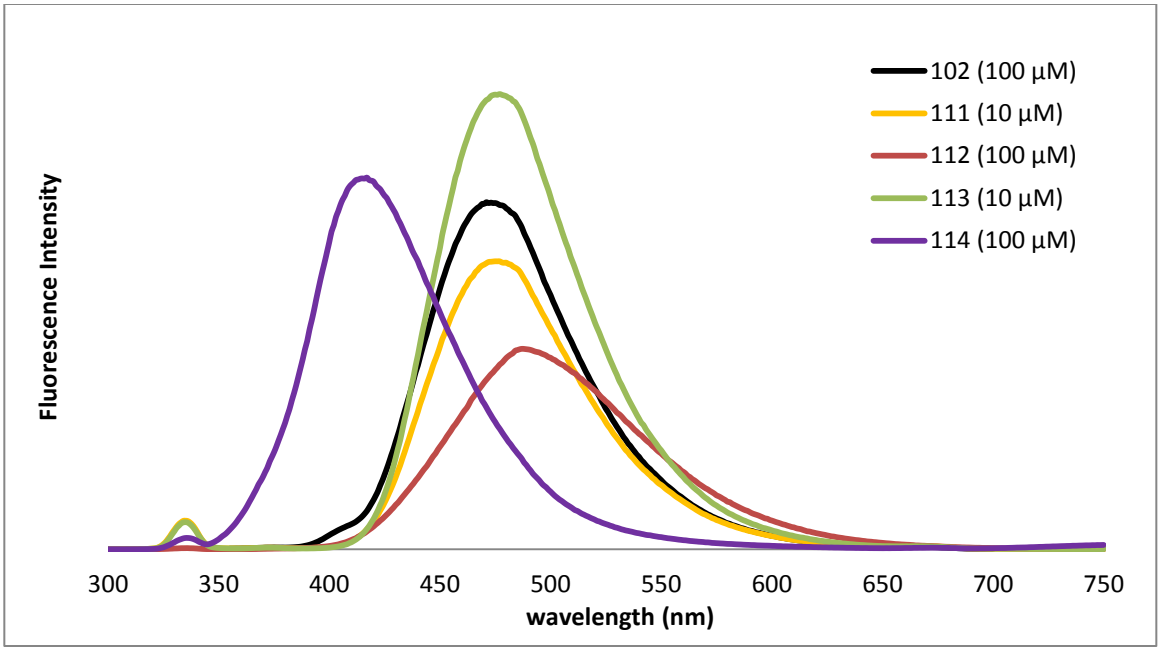


Figure 38. Fluorescence emission spectrum from excitation at 334 nm recorded for Group A (**102**, **111**, **112**, **113**, and **114)** as 100 µM or 10 µM solutions in EtOH at ambient temperature. Entry and exit slits set to 1 mm.

Similar to their absorbance maxima, **112** has a redshifted emission (λ_{em} = 487 nm, in EtOH) and **114** has a blue-shifted emission (λ_{em} = 414 nm, in EtOH). Given the unique absorbance profile for derivative **114**, which includes a broad absorption band at around 308 nm, as well as the presence of a second absorption band at around 370 nm, its fluorescence emission was analyzed at two additional excitation wavelengths (Figure 38), namely, 308 nm and 360 nm. Excitation at 308 nm resulted in the same emission wavelength as excitation at 334 nm (λ_{em} = 414 nm), which was expected given the two excitation wavelengths resided within the same absorption band.

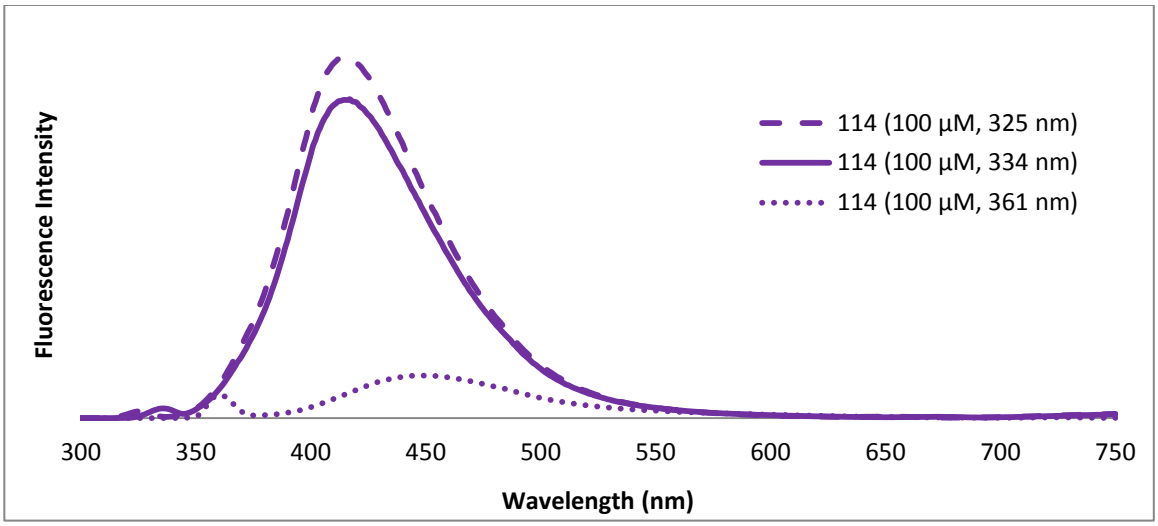


Figure 39. Fluorescence emission spectrum from excitation at 325 nm, 334 nm, and 361 nm, of a 100 µM solution of **114** in EtOH at ambient temperature. Entry and exit slits set to 1 mm.

Excitation at 360 nm, on the other hand, afforded an emission maximum at 448 nm, confirming the presence of a second absorption band. These results suggest that the two absorbance peaks correspond to two separate emissive states, though it is unknown if they arise from two different conformers or two different emissive states within the same conformation.

The UV/vis absorbance profiles for Group B are shown in Figure 39. Although each derivative does possess a maximum absorbance between 330-350 nm, their molar attenuation coefficients are considerably lower than those in Group A. This low absorptivity corresponded to weak fluorescence intensity upon excitation at 334 nm (Figure 40). Notably, **115**, **116**, and **104** all displayed nearly identical emission profiles, including fluorescence intensity and peak wavelength (λ_{max} = 468 nm, in EtOH). Derivative **98** shared similar maximum absorbance and emission wavelengths, though it

absorbed more strongly, with a much broader absorption band and higher intensity fluorescence.

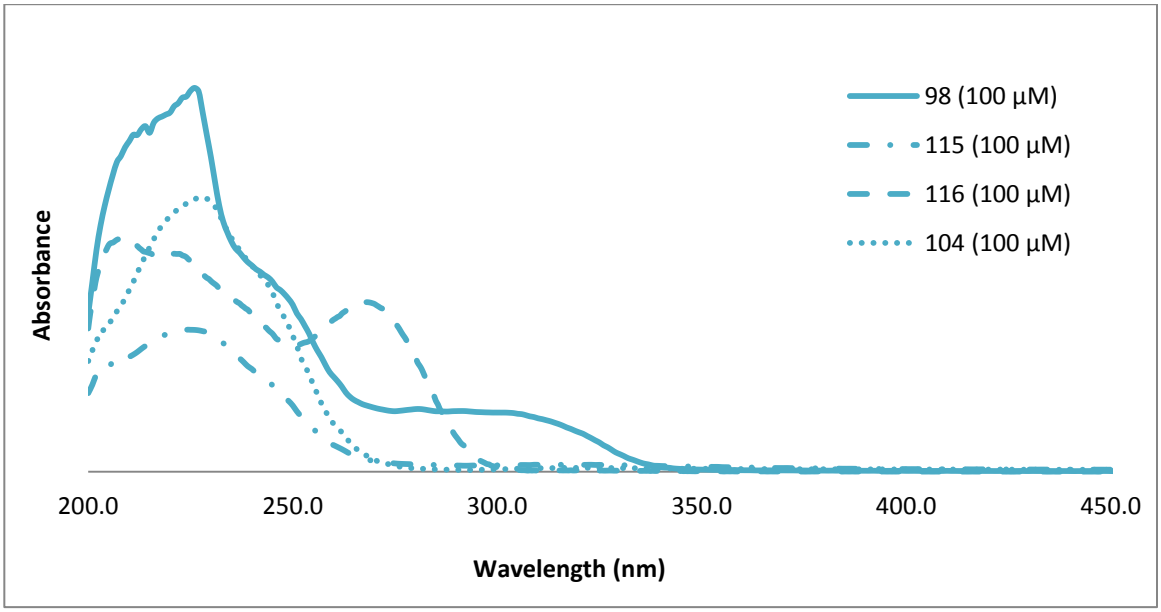


Figure 40. UV/Vis absorbance spectrum recorded for Group B (**98**, **115**, **116**, and **104**) as 10 µM solutions in EtOH at ambient temperature.

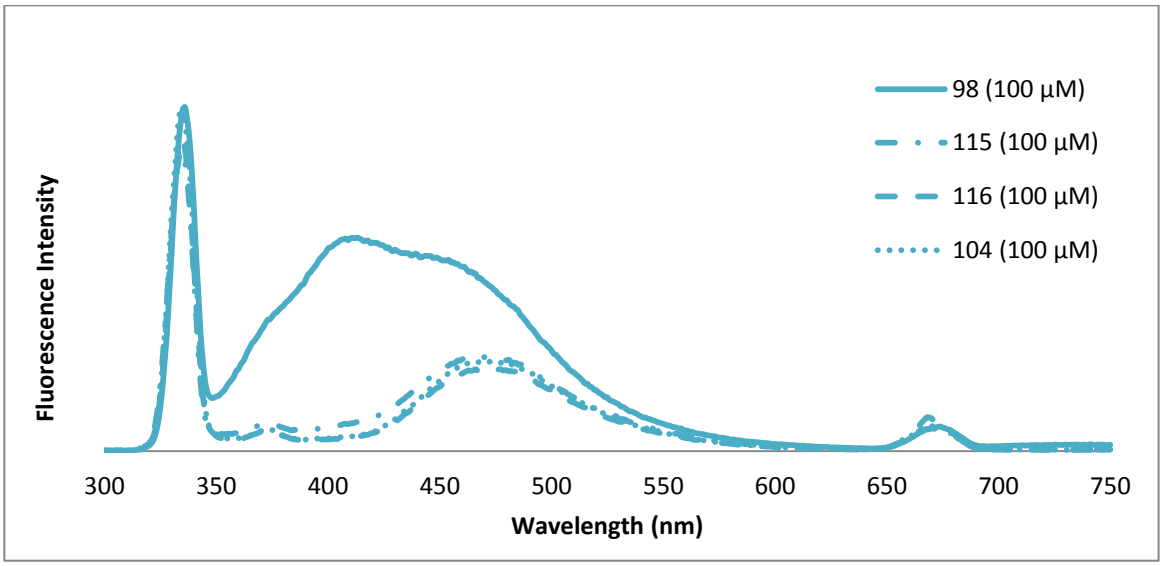


Figure 41. Fluorescence emission spectrum from excitation at 334 nm recorded for Group B (**98**, **115**, **116**, and **104**) as 100 µM solutions in EtOH at ambient temperature. Entry and exit slits set to 1 mm.

To further probe the electronic nature of these molecules, DFT calculations were carried out at the B3LYP 6-31G(d,p) level. Their optimized geometries, as well as the corresponding HOMO-1, HOMO, and LUMO are shown in Figure 41. In regards to the optimized geometries, no IHB was observed in the lowest energy structures (where applicable), except in the case of **115**, which did possess an IHB. However, when the chloride counter-ion was included in the geometry optimization, the IHB was superseded by a hydrogen bond to the halogen ion, consistent with previous results for **102**.

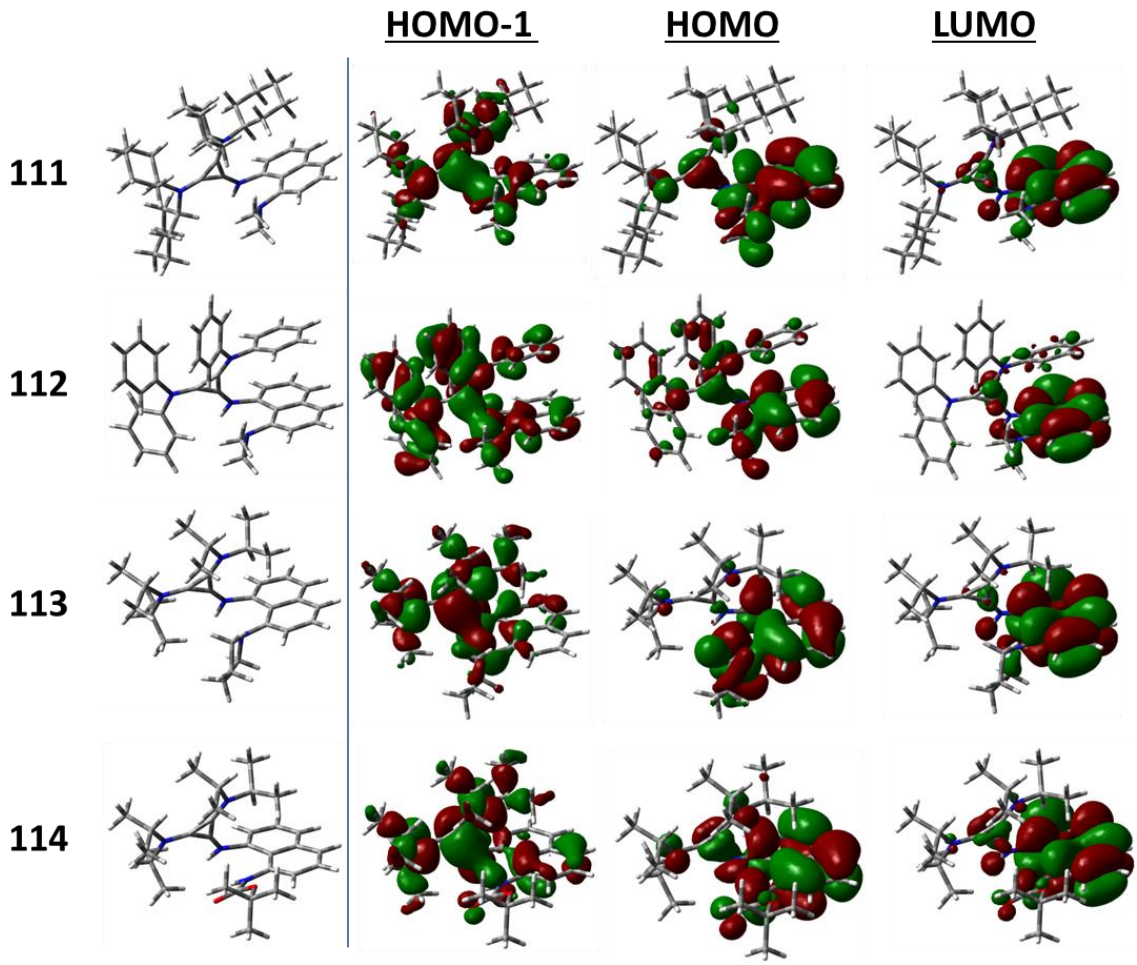


Figure 42. DFT calculated geometries and selected MOs for compounds **111**, **112**, **113**, and **114**.

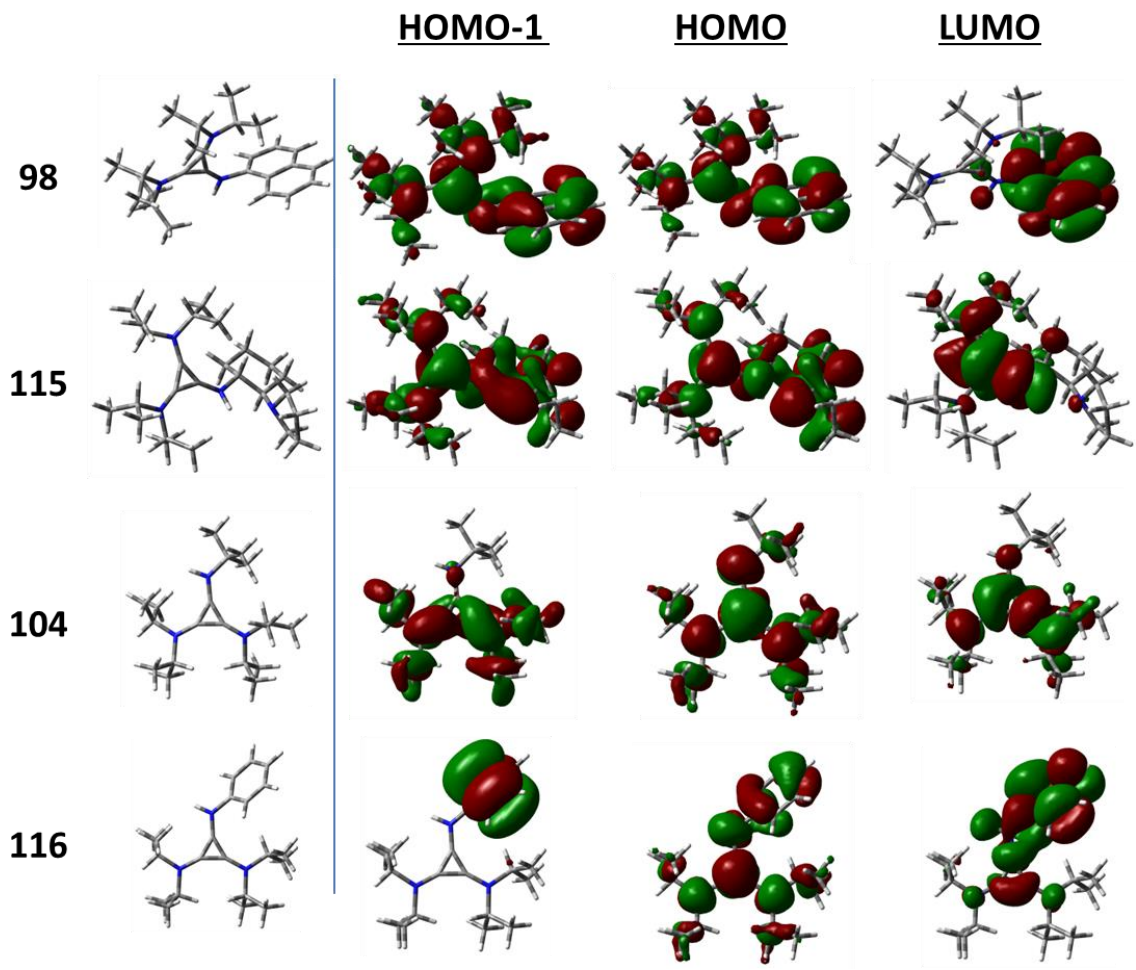


Figure 43. DFT calculated geometries and selected MOs for compounds **98**, **115**, **104**, and **116.**

Regarding the calculated molecular orbitals, the HOMO resides partly on the cyclopropenimine ring system of each derivative, with the exception of **113** wherein the HOMO is not delocalized onto the cyclopropenimine ring. Another common feature of these derivatives is that the HOMO-1 resides partly on the cyclopropenimine ring (although the HOMO-1 of **116** resides entirely on the phenyl ring, it possesses a nearly degenerate HOMO-2 that is on the cyclopropenimine ring). In the derivatives with an aromatic backbone, the LUMO resides mostly on the backbone, with a small contribution

from the cyclopropenimine ring. In those derivatives without an aromatic backbone (**115** and **104**), the LUMO resides predominantly on the cyclopropenimine core.

The key structural difference between Group A and Group B is the presence or absence of the proton-sponge (*i.e.*, aminonaphthalene) backbone. As such, and not surprisingly, the aminonaphthalene backbone plays an important role in the fluorescent profile of **102**. This agrees with the previous assertion that the electronic transitions of **102** are akin to those of DMAN (*i.e.*, originating from an NMe_2-based ^1L_a state followed by internal conversion to an emissive, naphthalene-based, $1\pi^*$ ICT state). This is further supported by comparing the spectroscopic profiles of **102** and **98**, which clearly demonstrate the importance of the NMe_2 substituent. Another similarity amongst the compounds in Group A is the strong orbital overlap observed in the HOMO-1 between the anilino-amine lone pair and the cyclopropenimine ring (Figure 41). This existence of this stabilizing interaction was further confirmed for all derivatives in Group A by NBO calculations. When previous studies on DMAN are considered, it is likely that this interaction plays a key role in the high fluorescence quantum yield observed in these derivatives. Previous work has shown that internal fluorescence quenching of *N*,*N*-dimethyl-1-aminonaphthalene (**110**) occurs through fast internal conversion resulting from twisting (geometry relaxation) of the dimethylamino group.[136] Furthermore, this same physical process has been implicated in the internal conversion of **5** and $\mathbf{5}H^+$, leading to both the fluorescent internal charge transfer state, as well as the non-radiative relaxation pathways.[137,138] More specifically the restricted motion of the dimethylamino groups in **5** and $\mathbf{5}H^+$ leads to a considerably lower energy excited state upon internal conversion and in turn a larger Stokes shift. On the other hand, increased vibrational

relaxation associated with the dimethylamino group leads to a low quantum yield. Based on the increased fluorescence intensity and quantum yield of **102**, it would appear that the ICT excited state established upon internal conversion is not as susceptible to non-radiative decay pathways through geometry reorganization. In all likelihood, this is a direct consequence of the observed HOMO-1 interaction, which restrains the anilino-amine lone pair in the excited state, as well as the ground state. This postulate is further supported by the increased quantum yield associated with **113** (0.43) compared to **102** (0.37), which is further restricted on account of its cyclic backbone. In addition to its role in geometrically constraining the amino group, the cyclopropenimine core likely affects the fluorescence profile more directly as well, through electronic contributions to the HOMO and/or LUMO. This can be seen not only in the visualized MOs, but also through the effect of the cyclopropenimine substituents (*i.e.*, **111** and **112**, Table 9) on the fluorescence excitation and emission wavelengths.

In conclusion, a set of cyclopropenimine containing compounds have been made, and their fluorescent nature investigated. It was discovered that the cyclopropenimine core possesses an absorption band in the ultraviolet region, and emits in the visible spectrum. Furthermore, when incorporated into the proton sponge manifold as an *N*-substituent, a substantial increase in fluorescence intensity and quantum yield was observed. This is believed to originate from entropic restriction of the dimethylamino substituent, through a strong interaction between the dimethylamino group and the cyclopropenimine ring in the excited state, which prevents non-radiative decay pathways. Changes to the electronic nature of the anilino-amine substituent or the cyclopropenimine's amino groups shift the absorption and emission wavelengths.

Electron withdrawing substituents on the cyclopropenimine ring resulted in a red-shifted absorption and emission, while electron withdrawing substituents on the anilino-nitrogen resulted in a blue-shifted absorption and emission. The fluorescent intensity, emission wavelength, and absorption wavelength of these small, organic molecules can be modified through functionalization. This new insight into the fluorescent nature of cyclopropenimine substituted proton sponges may prove useful for the ongoing development of this increasingly useful class of molecules.

Chapter 3 – Summary and Future Directions

3.1 - Summary of Results

The work presented herein has described the synthesis and theoretical investigation of cyclopropenimine containing compounds within the proton sponge backbone. Initially, the bis(dialkylamino)cyclopropenimine substituted proton sponge (**89**) was synthesized, and has provided new insight into the properties of bis(dialkylamino)cyclopropenimines and proton sponges. Among several notable aspects of this work was the introduction of a fourth factor in the basicity of a proton sponge, the generation of aromaticity. Subsequently, the bis-protonated sponge **90** was demonstrated to be an effective phase transfer catalyst for the alkylation of benzophenone glycinyl-imine **74**. Its catalyst function was studied, and was found to play a bifunctional role as a phase transfer agent and a hydrogen bond-catalyst. Next, a non-symmetric variant of proton sponge **89** was synthesized (**95**), and its pK_a measured experimentally. The experimentally measured pK_a closely matched a previously computed value obtained

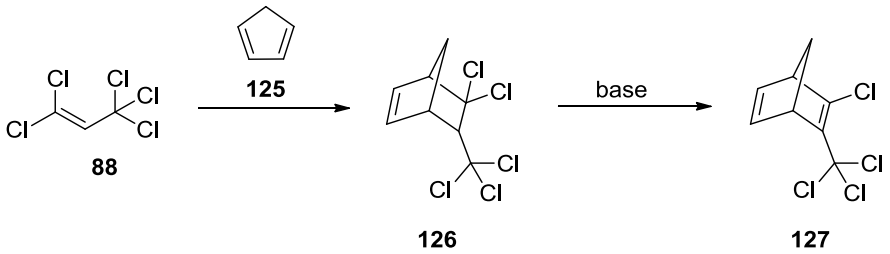
using DFT calculations. Furthermore, the protonated salt (**102**) was found to exhibit a rare "*in-out*" proton sponge geometry owing to a stabilizing interaction between the dimethylamine substituent and the cyclopropenimine ring. It was also discovered that **102** is highly fluorescent in nature, having a fluorescence quantum yield of 0.37 in 95% EtOH and a Stokes shift of 139 nm. Accordingly, a set of derivatives was synthesized in order to probe the fluorescent origins of **102** through structure-activity relationships. It was found that the cyclopropenimne unit is inherently fluorescent, absorbing in the UV region and emitting in the visible region. Additionally, when present on the proton sponge backbone, a cyclopropenimine unit stabilizes the adjacent *N*-dialkyl substituent and inhibits non-radiative relaxation pathways through geometry reorganization, thereby enhancing the fluorescence intensity and quantum yield.

3.2 - Future Directions

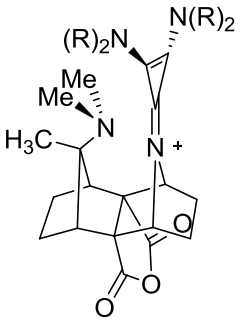
The application of DACN, **89**, or any bis-cyclopropenimine compound as a pincer ligand would be an obvious next step in this line of work. Preliminary work not reported herein has already proven its ability to bind a range of metals. Furthermore, DACs have already proven to be useful metal chelating ligands, and a bis-DAC has already been demonstrated to afford unique metal binding geometry (**71**, Figure 16). In addition to simple chelation, the proven susceptibility of DACs towards oxidation to radical dications could be exploited further in the context of metal chelating ligands for spintronics systems and single molecule magnets.

A tangential application of this work would be utilizing by-product **88** obtained from thermal rearrangement of **51** as a novel organic building block. Surprisingly, to date there has been no report of **88** being used as a starting material for any chemical reaction. In particular, **88** would represent a very useful dienophile in Diels Alder chemistry Scheme 27). For instance, the reaction between **88** and cyclopentadiene (**125**) would afford the highly functionalized, asymmetric compound, **126**. Not only would **126** be a good building block for natural product synthesis, but elimination of a chlorine atom would afford **127**, which could be explored further as a η2, π-type, asymmetric metal chelating ligand.

Scheme 27. Synthetic strategy towards new organic building blocks **126** and **127** based on by-product **88** via Diels Alder reaction with cyclopentadiene (**125**).



Lastly, the interaction between an electron donor and a cyclopropenimine unit observed in the Janus sponge should be investigated further. The nature of this interaction is still largely unknown. Though only one specific utility of this interaction was demonstrated in this work, exploring the nature of this type of interaction could prove fruitful. As such, the synthesis of a derivative such as **128** (Figure 43) would prove informative.



128

Figure 44. Proposed, highly constrained cyclopropenimine derivative.

Furthermore, by applying the concept of Verkade's base (Figure 3), a compound such as **129** or **131** (Figure 44) could be made to look at pH dependent conformational changes, and the strength and stability of N_{LP}-cyclopropenimine donor-acceptor interactions.

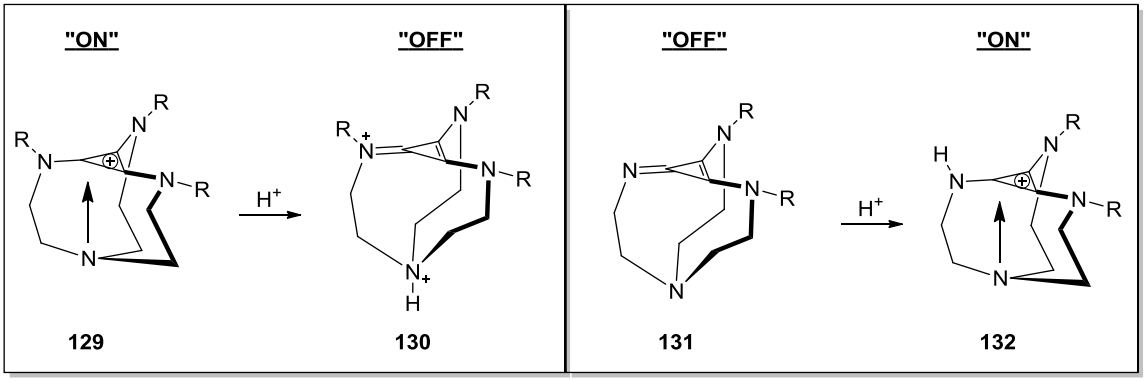


Figure 45. Proposed cyclopropenimine derivative based on Verkade's base.

It is possible that this newly discovered donor-acceptor interaction could lead to new chemical reactivity, molecular switches, or compounds with unique fluorescent properties.

Appendix A

Calculating K_c and $\Delta G^{\ddagger}$ using variable temperature NMR:

$K_c = \frac{\pi \Delta \nu}{\sqrt{2}}$, where $\Delta \nu$ is the maximum width between the two peaks.

$\Delta G^{\ddagger} = RT_c [22.96 + \ln (T_c/\Delta \nu)]$, where T_c is the coalescence temperature.

NBO theory:

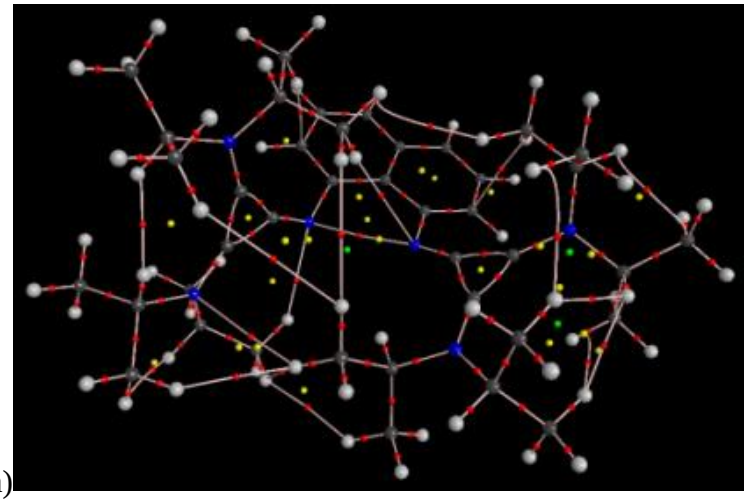
Natural bond orbital (NBO) theory is the mathematical formalism that describes the unique set of orthogonal, one-electron functions (orbitals) inherent to a particular *N*-electron wavefunction, which are known as natural atomic orbitals (NAO). The NAOs are atom centered orbitals that differ from traditional atomic orbitals by including the effect of the surrounding chemical environment. Calculation of NAOs are occupancy-weighted, favoring orbitals with the highest possible occupancy, thus providing a "Lewis-type" description of the molecule. By combining these NAOs into maximum occupancy, two-electron orbitals (these are the NBOs) through variational optimization, a Lewis-type description of the molecule is obtained, which describes core orbitals, lone pairs, and bonding interactions within the computed wavefunction. This allows programs to extract fundamental concepts regarding atomic hybridization and bonding interactions within a given molecule. NBO programs also compute energies associated with orbital overlap (*i.e.*, donor-acceptor interactions) between any set of high occupancy bonding NBOs (the donor), and low-occupancy antibonding NBOs (the acceptor). The strength of these donor-acceptor interactions is determined by their associated stabilization energy,

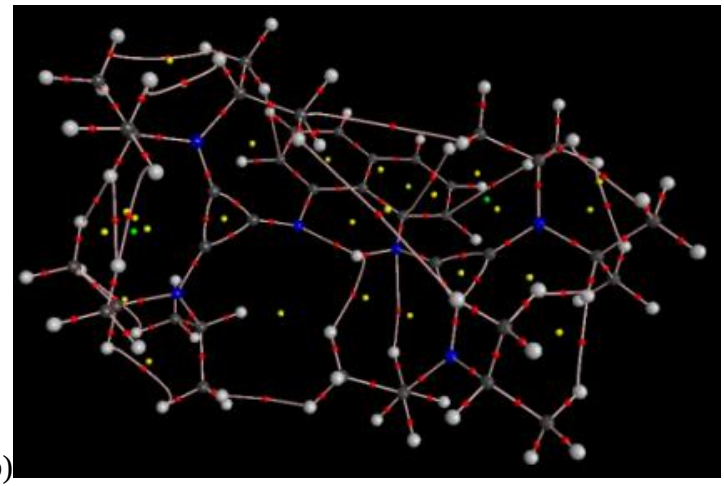
reported as E_{NBO} in values of kcal/mol. The E_{NBO} values are not chemically accurate, but can be used to confirm the existence of a bonding interaction and to compare the relative strength of bonding interactions.

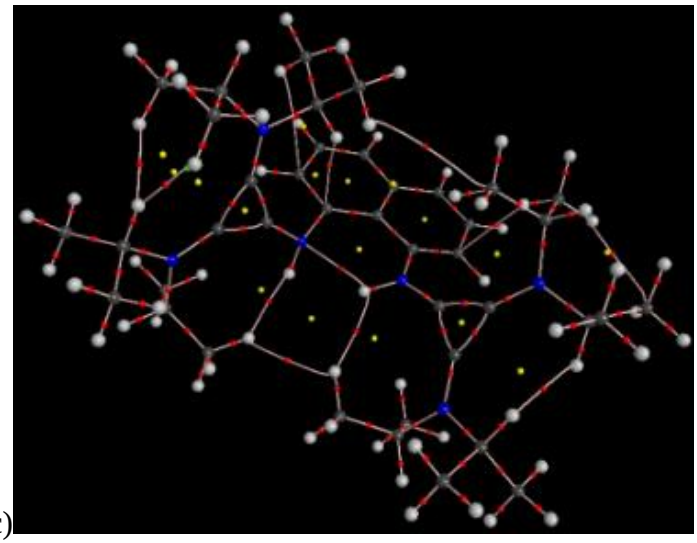
AIM theory:

Bader's theory of Atoms in Molecules (AIM), also known as Bader's Quantum Theory of Atoms in Molecules (QTAIM) is a method of evaluating a computed wavefunction by analysing the topology of the electron density, $p(\boldsymbol{r})$. AIM analysis searches for "critical points" associated with the electron topology to gain useful chemical information about the system. A critical point is a maximum, minimum, or a saddle point of electron density. Critical points are characterized by two numbers, rank (ω, the number of non-zero curvatures) and signature (σ, the sum of their algebraic signs), and are denoted by (ω, σ). Thus, when three curvatures are present (which is almost always the case) and two curvatures are negative ($p(\boldsymbol{r})$ is a maximum at the critical point in the plane defined by the two associated axes), while the third curvature is positive ($p(\boldsymbol{r})$ is a minimum at the critical point along the axis perpendicular to this plane), the critical point is termed a bond critical point (BCP). In other words, if a critical point along a path of electron density links two nuclei, and is a maximum of electron density in all directions perpendicular to this line, it is a BCP. A BCP is indicative of a bonding interaction between two atoms because the accumulation of electric charge between a pair of nuclei is a necessary and sufficient condition for two atoms to be bonded together.

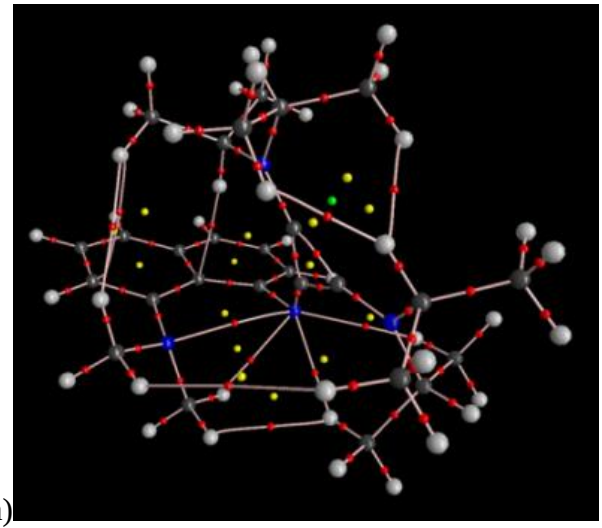
AIM Structures of **89** (a), **91** (b), and **90**$_{\mathbf{opt}}$ (c).

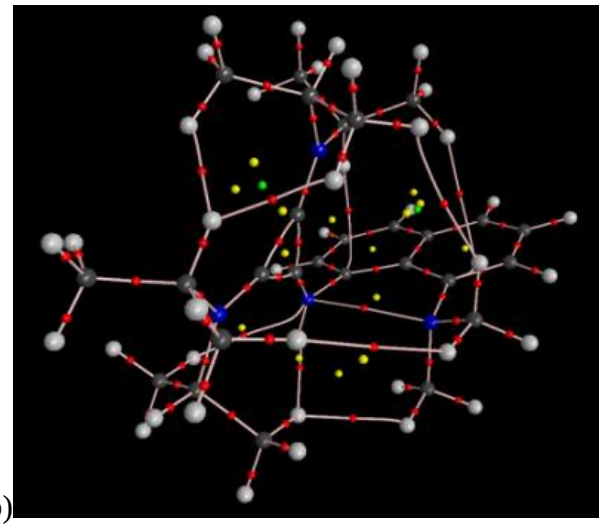
a) 

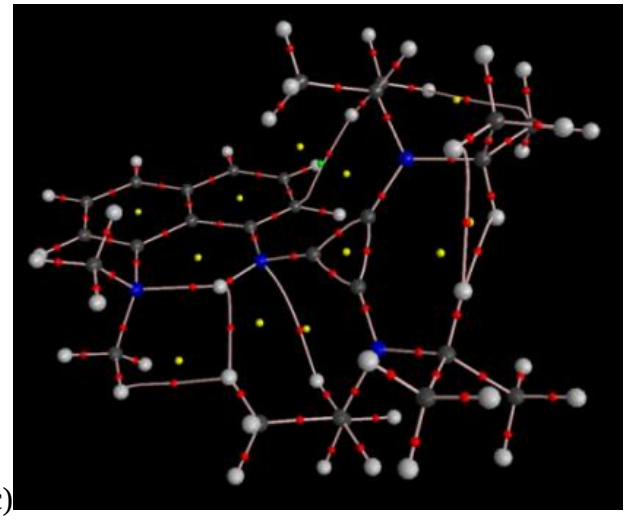
b) 

c) 

QTAIM Structures of **95** (a), **102**$_{xray}$ (b) and **102**$_{opt}$ (c).

a) 

b) 

c) 

Appendix B

Relative pK_a calculations

For a representative example of a relative computational pK_a calculation: The pK_a of **89** was computed relative to that of TMGN (**34**), using the Equation (B2), as follows:

$$pK_a = \Delta G°_{base} /2.303RT \qquad \textit{Eq. (B1)}$$

$$\Delta pK_a = [G°(\mathbf{89})_{MeCN} - G°(\mathbf{91})_{MeCN} + G°(\mathbf{35})_{MeCN} - G°(\mathbf{34})_{MeCN}\ ] / 2.303RT \qquad \textit{Eq. (B2)}$$

(where $G°(\mathbf{X})_{MeCN}$ is the computed Gibbs free energy species **X** in acetonitrile)

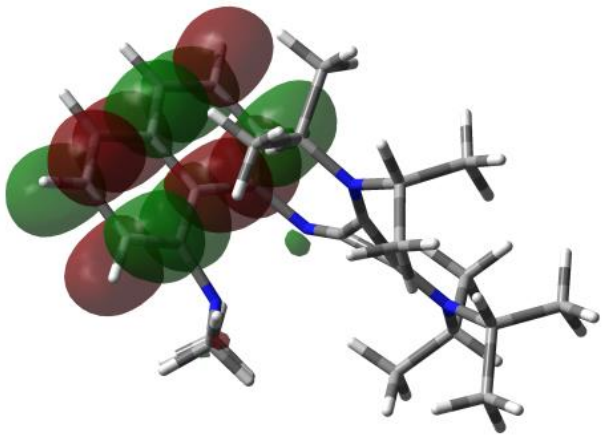
Since the pK_a of **34** has been measured to be 25.1, and the ΔpK_a obtained from Equation (B2) was found to be 1.9, the predicted pK_a using this methodology is 27.

Experimental procedure for pK_a measurement

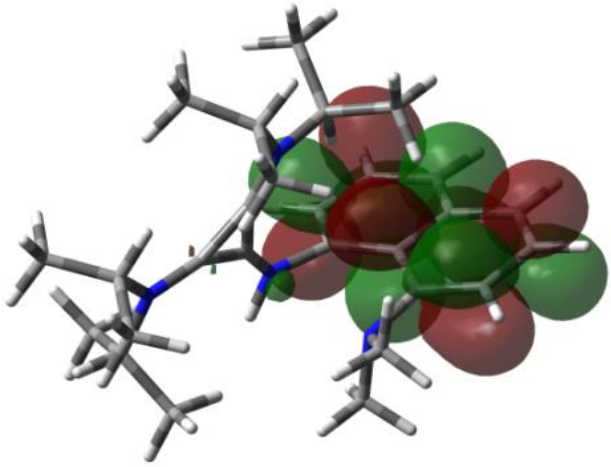
Compound **95** (8.6 mg, 0.025 mmol, 1 equiv.) and 1,1,3,3-tetramethylguanidine TMG (3.0 μL, 0.025 mmol, 1 equiv) were dissolved in 0.6 mL MeCN-d_3. The ^{1}H NMR chemical shift of the isopropyl groups belonging to **95** in this mixture was compared against those in pure **95** and **102** to estimate the equilibrium ratio and equilibrium constant of the reaction. The equilibrium constant was then used, with the known pK_a of TMG (23.3) to determine the pK_a of **95**. The experiment was performed using two different methods; combining the freebase **95** and the hydrochloride salt of TMG, and combining the hydrochloride salt **95** and the freebase, TMG. Each of these two procedures was repeated in triplicate and a representative ^{1}H NMR spectrum of each is included (page 171-173).

Appendix C

B3LYP/6-31G(d,p) computed LUMO+1 of ***95*** *(a) and* $\boldsymbol{102_{xray}}$ *(b).*



a)



b)

Quantum yield measurement and calculation:

Quantum yields (ϕ) were measured in 95% ethanol, relative to that of anthracene.[139] Emission spectra for the quantum yield calculation were acquired using quartz cuvettes in a fluorescence spectrophotometer with a Xenon flash lamp at ambient temperature. Sample and standards were prepared as $1x10^{-5}$ M solutions in 95% ethanol. Entrance and exit slit widths were set to 5 mm, and the excitation wavelength was 333 nm for both the

standard and sample. Quantum yields were calculated using Equation C1, according to the 2011 IUPAC technical report on standards for photoluminescence quantum yield measurements in solution.[140]

$$\phi_f^x = \frac{F^x f_{st} n_x^2}{F^{st} f_x n_{st}^2} \phi_f^{st} \qquad \text{[Equation C1]}$$

Were ϕ_f^x and ϕ_f^{st} are the quantum yields of the sample and the standard, respectively. $F^x$and $F^{st}$are the integrated fluorescence intensities of sample and standard spectra. f_x and f_{st} are the absorption factors of the sample and standard at the excitation wavelength (where $f = 1 - 10^{-A}$, and A = absorbance). n_x and n_{st} are the refractive indices of the sample and reference solution, respectively, which were assumed to be the same in this experiment.

Experimental Section

Materials and Methods:

Materials were obtained from commercial suppliers and were used without further purification, unless otherwise specified. Dichloromethane (DCM) was distilled over CaH, tetrahydrofuran (THF) was distilled over Na and a benzophenone indicator, and Acetonitrile (MeCN) was distilled over Na_2CO_3. Reactions were monitored by thin layer chromatography (TLC) using TLC silica gel 60 F254. NMR spectra were obtained with a 300 MHz spectrometer (^{1}H 300 MHz, ^{13}C 75.5 MHz or ^{13}C 150.9 MHz, ^{19}F 292.4 MHz, ^{11}B 96.3 MHz) or a 400MHz spectrometer. The chemical shifts are reported as δ values

(ppm) relative to tetramethylsilane. All reactions were performed under an inert nitrogen atmosphere. FT-IR spectra were obtained with an attenuated total reflectance spectrophotometer from neat samples. HRMS (high-resolution mass spectrometry) spectra were measured using electrospray ionization (ESI) or fast atom bombardment (FAB) and a time-of-flight (TOF) mass analyzer in positive ionization mode. Absorption spectra were measured using a UV-Vis-NIR spectrophotometer at ambient temperature. Emission spectra were obtained on a Xenon flash lamp fluorescence spectrophotometer at ambient temperature with entrance and exit slit widths set to 5 mm.

Computational Methodology:

Calculations were carried out using Kohn-Sham hybrid-Density Functional Theory (DFT) at the level of theory specified for each individual calculation. Geometry optimization, vibrational frequency analysis, molecular orbital visualizations were performed using the Gaussian 09 and GaussView v5.0.8 programs[141] at standard temperature and pressure. Natural bond orbital analysis (NBO Version 3.1[142] as implemented in Gaussian 09) was used to quantify the electronic donor-acceptor interactions as second-order perturbation energies (E_{NBO}).To account for solvent effects, the Integrated Equation Formalism Polarized Continuum Solvation Model (IEFPCM)[143] was used throughout the computations with default parameters for the chosen solvent(s). Transition states were confirmed by the presence of a single imaginary frequency and the Intrinsic Reaction Coordinate (IRC) methodology[144] was then implemented to identify the corresponding minima, which were confirmed by the presence of only real vibrational frequencies. QTAIM calculations were computed using AIM2000.[145] Mercury 3.1[146] was used to compute the plane angles. Ortep-3 v. 1.0.3[147] was used to render the x-ray crystal

structures. Maestro v. 9.8[148] was used to generate the hydrophilic/hydrophobic surface plots.

Synthetic protocols:

Pentachlorocyclopropane (**51**):[149]

A 250 mL RBF containing a stir bar and sodium trichloroacetate (32 g, 0.173 mol), was fitted with a reflux condenser, thoroughly flame-dried, and then backfilled with $N_{2(g)}$. Trichloroethylene (50ml, 0.56 mol), followed by 1,2-dimethoxyethane (7.5ml), were then added via syringe. The reaction was heated to reflux in an oil bath between 90-95 °C and stirred for 72 hours. The reaction was then removed from the oil bath and allowed to settle, at which point the top organic layer (dark brown oil) was decanted. The remainder was washed with H_2O (100 ml) and the organic layer extracted using a separatory funnel. The organic extract were combined and dried over $MgSO_4$. Vacuum distillation with gradual heating up to 90 °C afforded **51** as a clear and colourless liquid in 42% yield (15.2 g, 0.071 mol) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 1H).

Tetrachlorocyclopropene **(52):[150]**

Pentachlorocylopropane, **51** (15.2g, 0.071 mol) was slowly added to a stirring solution of 18M KOH (10ml). The reaction proceeded for three hours at room temperature. The ensuing reaction mixture was diluted with H_2O (20mL) and acidified to a pH 1 using concentrated hydrochloric acid (12M, 13 mL). The organic layer was extracted three times with 10 mL DCM, and the combined extracts dried over $MgSO_4$ and concentrated *in vacuo*. Distillation into a receiving flask kept at -78 °C afforded **52** in 89% yield (11.2

g, 0.063 mol). ^{1}H NMR showed no signal, IR = 1810 (w), 1300 (w), 1190 (w), 1148 (s), 1100 (w), 1055 (s), 817 (w), 753 (b), 690 (m, s) 617 (s), 412 (s).

1,8-bis(bis(diisopropylamino)cyclopropenium)naphthalene chloride, 90:

To a solution of tetrachlorocyclopropene, **52** (0.025 mL, 0.2 mmol), in dichloromethane (2 mL) was added freshly distilled diisopropylamine (0.11 mL, 0.8 mmol), dropwise under an inert nitrogen atmosphere. The reaction was stirred for four hours at room temperature, after which 1,8-diaminonapthalene (16 mg, 0.1 mmol) was added in a single portion, and the reaction was stirred for an additional 16 hours. The crude product was recrystallized from acetonitrile and benzene to afford **90** as white needles in ca. 42% yield (59 mg, 0.08 mmol). m.p. = 225°C - 230°C. Subsequent X-ray quality single crystals were grown from ethyl acetate and acetonitrile. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.32 (s, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.19 (d, J = 7.2 Hz, 2H), 3.76 (m, 8H), 1.30 (d, J = 6.7 Hz, 48H). ^{13}C NMR (75 MHz, CDCl3): δ = 136.7, 135.2, 128.4, 126.0, 125.5, 124.6, 116.6, 114.0, 51.20, 22.30. HRMS (FAB): m/z calcd for $C_{40}H_{63}N_6$ ([M-H]+): 627.5109, found: 627.5114.

Counterion exchange to provide 1,8-bis(bis(diisopropylamino)cyclopropenium) naphthalene tetrafluoroborate, 90•BF_4:

To a solution of **90** (140 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere, was added solid $NaBF_4$ (26 mg, 0.24 mmol). The resulting solution was stirred for four hours. Subsequently, 5 mL of water was added, and the two phases separated. The aqueous layer was then extracted three times with 5 mL dichloromethane

and the combined organic layers dried over $MgSO_4$ to afford **90•BF_4** as a white solid in ca. 95% yield (152 mg, 0.19 mmol). m.p. = 235°C–240°C. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 10.39 (s, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.1 Hz, 2H), 3.69 (m, 8H), 1.27 (d, *J* = 6.5 Hz, 48H) ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 136.5, 135.1, 128.0, 126.0, 125.4, 124.7, 117.0, 113.6, 51.0, 22.1. HRMS (FAB): m/z calcd for $C_{40}H_{63}N_6$ ([M-H]+): 627.5109, found: 627.5114.

Synthesis of 1,8-bis(bis(diisopropylamino)cyclopropenimine)naphthalene, 89:

To a suspension of **90** (35 mg, 0.05 mmol) in toluene (2 mL) under an inert atmosphere, was added dry potassium bis(trimethylsilyl)amide (KHMDS, 0.5M in toluene (0.5 mL, 0.25 mmol), dropwise. The reaction was stirred for two hours. The volatile components were removed under reduced pressure, and the product was extracted with hot hexane. The resulting product was isolated as orange crystals in ca. 80% yield (25 mg, 0.04 mmol). m.p. = 145°C–150°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31 (m, 4H), 6.49 (dd, *J* = 5.9, 2.8 Hz, 2H), 3.84 (m, 8H), 1.30 (d, *J* = 6.9 Hz, 48H) ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 146.0, 136.8, 125.8, 120.6, 120.3, 118.4, 117.6, 113.0, 50.9, 22.23. HRMS (FAB): m/z calcd for $C_{40}H_{63}N_6$ ([M+H]+): 627.5109, found: 627.5114.

General Phase Transfer Catalysis procedure for the synthesis of 101a-101m:

N-(Diphenylmethylene)glycine *tert*-butyl ester **74**, (25 mg, 0.0846 mmol, 1 equiv.), DACN 2HCl (**90**) (3 mg, 0.0043 mmol, 5 mol%), and electrophile (0.01 mmol, 1.2 equiv.) was dissolved in 0.5 mL of dichloromethane in a 10 mL vial with a stir bar, followed by the addition of 0.5 mL of 50% aqueous potassium hydroxide. The vial was

closed and the reaction was allowed to stir at room temperature for one hour. The reaction was extracted with 3 aliquots of 2 mL dichloromethane, the organic layer was dried with magnesium sulfate, and concentrated *in vacuo*. Products were isolated using flash column chromatography with the specified solvent mixture.

tert-butyl-2-(diphenylmethyleneamino)-3-(phenyl)propanoate (101a): [151]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (hexanes: ethyl acetate: triethylamine). The final product was obtained as white crystals in 92% yield (0.078 mmol, 30 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, J = 7.4 Hz, 1H), 7.61 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.27-7.39 (m, 5H), 7.19–7.21 (m, 2H), 7.07–7.10 (m, 2H), 6.63 (d, J = 7.0 Hz, 2H), 4.14 (dd, J = 9.6, 4.0 Hz, 1H), 3.19-3.28 (m, 2H), 1.47 (s, 9H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.2, 139.7, 138.3, 137.6, 132.4, 130.0, 129.8, 128.7, 128.2, 128.0, 127.96, 127.69, 126.1, 81.1, 67.9, 39.6, 28.0.

tert-butyl-2-(diphenylmethyleneamino)-3-(naphthalen-2-yl)propanoate (101b): [151]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine).The final product was obtained as yellow oil in 92% yield (0.078 mmol, 34 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.85 (m, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.51–7.60 (m, 4H), 7.41–7.44 (m, 2H), 7.29–7.35 (m, 3H), 7.16–7.24 (m, 2H), 6.56 (d, J = 7.2 Hz, 2H), 4.27 (dd, J = 9.0, 4.4 Hz, 1H), 3.35–3.42 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.4, 139.5,

137.7, 136.3, 135.9, 133.4, 132.4, 132.1, 130.0, 128.7, 128.4, 128.2, 128.0, 127.9, 127.6, 127.5, 127.4, 125.7, 125.2, 81.2, 67.9, 39.7, 28.0.

tert-butyl-2-(diphenylmethyleneamino)-3-(phenyl)butanoate (101c): [152]

Compound was purified via gravity column chromatography, using a mixture of 97:2:1 (Hexanes : Ethyl Acetate : Triethylamine). The final product was obtained as yellow oil 91% yield (0.077 mmol, 31 mg). ^{1}H NMR (300 MHz, $CDCl_3$): 7.66 (d, *J* = 6.8 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 2H), 7.30–7.40 (m, 5H), 7.14–7.25 (m, 5H), 6.77 (d, *J* = 6.8 Hz, 2H), 4.01 (d, *J* = 8.2 Hz, 1H), 3.49–3.61 (m, 1H), 1.45 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 170.4, 143.8, 143.4, 136.6, 136.4, 132.4, 130.1, 130.0, 129.97, 128.9, 128.8, 128.6, 128.3, 128.27, 128.23, 128.14, 128.14, 128.0, 127.9, 127.88, 127.82, 127.7, 126.2, 81.0, 80.8, 72.8, 71.9, 43.5, 28.0, 27.8, 18.0, 16.82.

tert-butyl-2-(diphenylmethyleneamino)-3-(phenyl)propanoate (101d = 101a): [154]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as white crystals in 60% yield (0.051 mmol, 19 mg).^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, J = 7.4 Hz, 1H), 7.61 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.27–7.39 (m, 5H), 7.19–7.21 (m, 2H), 7.07–7.10 (m, 2H), 6.63 (d, J = 7.0 Hz, 2H), 4.14 (dd, J = 9.6, 4.0 Hz, 1H), 3.19–3.28 (m, Hz, 2H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.2, 139.7, 138.3, 137.6, 132.4, 130.0, 129.8, 128.7, 128.2, 128.0, 127.96, 127.69, 126.1, 81.1, 67.9, 39.6, 28.0.

***tert*-butyl-2-(diphenylmethyleneamino)-3-(4-methylphenyl)propanoate (101e):** [153]

Compound was purified via gravity column chromatography, using a mixture of 97:2:1 (Hexanes : Ethyl Acetate : Triethylamine). The final product was obtained as clear oil in 92% yield (0.078 mmol, 31 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.27–7.39 (m, 6H), 6.99 (dt, *J* = 8.7, 7.5 Hz, 4H), 6.65 (d, *J* = 7.0 Hz, 2H), 4.11 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.09–3.25 (m, 2H), 2.31 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9, 170.1, 139.6, 136.4, 135.5, 135.2, 130.0, 129.7, 128.7, 128.2, 128.1, 128.0, 127.9, 127.7, 81.05, 68.0, 39.1, 28.0, 21.0.

***tert*-butyl-2-(diphenylmethyleneamino)-3-(4-chlorophenyl)propanoate (101f):** [154]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as clear oil in 91% yield (0.077 mmol, 32 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, J = 6.8 Hz, 2H), 7.30–7.40 (m, 6H), 7.18 (d, J = 6.8 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 7.0 Hz, 2H), 4.11 (dd, J = 8.7, 4.2 Hz, 1H), 3.10–3.24 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6, 170.5, 139.4, 137.6, 136.2, 132.4, 132.0, 131.2, 130.7, 130.2, 130.0, 128.7, 128.4, 128.2, 81.3, 67.6, 38.9, 28.0.

***tert*-butyl-2-(diphenylmethyleneamino)-3-(4-nitrophenyl)propanoate (101g):** [155]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as white crystals in 93% yield (0.079 mmol, 34 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, J = 6.9 Hz, 2H), 7.58 (d, J = 6.9 Hz, 2H), 7.25–7.36 (m, 8H), 6.73 (d, J = 6.9 Hz,

2H), 4.19 (dd, J = 8.0, 2.3 Hz, 1H), 3.30–3.33 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9, 170.1, 146.6, 146.5, 139.1, 136.0, 130.6, 130.4, 128.7, 128.6, 128.3, 128.1, 127.5, 123.2, 81.7, 67.0, 39.4, 28.0.

tert-butyl-2-(diphenylmethyleneamino)-3-(4-methoxyphenyl)propanoate (101h):[154]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as clear oil in 54% yield (0.046 mmol, 19 mg). ^{1}H NMR (300 MHz, $CDCl_3$): 7.47–7.85 (m, 10 H), 7.38 (d, *J* = 4.0 Hz, 2H), 7.02 (d, *J* = 6.0 Hz, 2 H), 4.12 (t, *J* = 4.0 Hz, 1H), 3.77 (s, 3 H), 3.10–3.25 (m, 2 H), 1.47 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9, 170.2, 160.1, 136.4, 132.4, 130.8, 130.1, 129.4, 128.7, 128.5, 128.2, 128.0, 127.8, 127.7, 81.0, 68.1, 55.2, 38.7, 28.0.

tert-butyl-2-(diphenylmethyleneamino)-5-(phenyl)pentanoate (101i):[156]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as clear oil in 10% yield (0.0085 mmol, 4 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 6.8 Hz, 2H), 7.44–7.46 (m, 3H), 7.32–7.41 (m, 4H), 7.14–7.19 (m, 5H), 3.97 (t, J = 6.4 Hz, 1H), 2.59 (t, J = 7.8 Hz, 2H), 1.94–2.01 (m, 2H), 1.59–1.69 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.5, 169.9, 142.2, 139.7, 136.7, 130.1, 128.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 125.7, 80.8, 65.9, 35.6, 33.3, 28.1, 27.8.

tert-butyl-2-(diphenylmethyleneamino)pent-4-enoate (101j):[155]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as clear oil in 91% yield (0.077 mmol, 26 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 6.8 Hz, 2H), 7.31–7.46 (m, 6H), 7.17–7.21 (m, 2H), 5.69–5.79 (m, 1H), 5.01–5.12 (m, 2H), 4.03 (dd, J = 7.7, 2.0 Hz, 1H), 2.62–2.69 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.1, 139.7, 136.6, 134.7, 132.4, 130.1, 130.0, 128.8, 128.5, 128.2, 117.2, 81.0, 65.8, 38.1, 28.0.

tert-butyl-2-(diphenylmethyleneamino)pent-4-enoate (101k =101j): [157]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as clear oil in 89% yield (0.075 mmol, 25 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 6.8 Hz, 2H), 7.31–7.46 (m, 6H), 7.17–7.21 (m, 2H), 5.69–5.79 (m, 1H), 5.01–5.12 (m, 2H), 4.03 (dd, J = 7.7, 2.0 Hz, 1H), 2.62–2.69 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.1, 139.7, 136.6, 134.7, 132.4, 130.1, 130.0, 128.8, 128.5, 128.2, 117.2, 81.0, 65.8, 38.1, 28.0.

tert-butyl-2-(diphenylmethyleneamino)hex-4-enoate (101l): [156]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as clear oil in 91% yield (0.077 mmol, 27 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 6.8 Hz, 2H), 7.34–7.46 (m, 6H), 7.16–7.19 (m, 2H), 5.31–5.33 (m, 2H), 3.98 (dd, J = 7.6, 2.0 Hz, 1H), 2.53–2.62 (m, 2H), 1.64 (d, J = 6.1 Hz, 3H), 1.46 (s, 9H). ^{13}C NMR (75

MHz, $CDCl_3$): δ = 171.1, 169.8, 139.8, 136.8, 130.1, 128.8, 128.4, 128.3, 128.0, 127.95, 127.93, 127.8, 127.1, 126.1, 80.8, 66.4, 36.9, 28.0, 17.9.

(E)-tert-butyl 2-((diphenylmethylene)amino)-5-phenylpent-4-enoate **(101m):** [158]

Purified compound was eluted via gravity column chromatography, using a mixture of 97% : 2% : 1% (Hexanes: Ethyl Acetate: Triethylamine). The final product was obtained as a viscous white oil in 90% yield (0.070 mmol, 24 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 6.8 Hz, 2H), 7.31–7.46 (m, 6H), 7.16–7.45 (m, 13H), 6.40–6.46 (m, 1H), 6.08–6.16 (m, 1H), 4.09–4.13 (m, 1H), 2.77–2.85 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9, 170.3, 139.7, 137.5, 136.7, 132.4, 130.2, 128.8, 128.5, 128.4, 128.0, 127.9, 127.0, 126.5, 126.0, 81.1, 66.2, 37.3, 28.1.

2-(fluoromethyl)naphthalene **(106):**[54a]

Under a dry, inert atmosphere, *2-(bromomethyl)naphthalene*, **100b**, (25 mg, 0.085 mmol, 1 equiv.), **89** (3 mg, 0.004 mmol), and potassium fluoride (581 mg, 0.01 mmol) was dissolved in acetonitrile (0.5 mL) in a 10 mL vial with a stir bar, followed by the addition of 0.5 mL of 50% aqueous potassium hydroxide. The vial was closed and the reaction was allowed to stir at room temperature for one hour. The reaction was extracted with 3 aliquots of 2 mL dichloromethane; the organic layer was dried with magnesium sulfate, and concentrated *in vacuo*. The product was purified using flash column chromatography 9:1 (Hexane: Ethyl Acetate). The final product was obtained as a viscous white oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.95 (m, 4H), 7.55–7.58 (m, 3H), 5.67 (s, 1H), 5.51 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.8, 133.6, 133.4 (d, *J* = 1.9 Hz), 133.2,

128.1, 127.8, 126.8 (d, *J* = 7.5 Hz), 126.5 (d, *J* = 5.7 Hz), 125.0 (d, *J* = 4.5 Hz), 84.8 (d, *J* = 2.0 Hz). ^{19}F NMR (292 MHz, $CDCl_3$): δ = -206.4.

tert-butyl (8-aminonaphthalen-1-yl)carbamate (107).[159]

To a flame dried 100 mL round bottom flask backfilled with $N_{2(g)}$ was added 1,8-diaminonaphthalene (2.0 g, 12.6 mmol), followed by the addition of THF (40 mL) and NEt_3 (2 mL, 27.2 mmol). To the resulting mixture a solution of di-*tert*-butyl-dicarbonate (3.0 g, 13.9 mmol) in THF (10 mL) was added drop-wise over two hours *via* syringe pump and allowed to stir at room temperature for 18 hours. THF was removed under reduced pressure and the crude product mixture was dissolved in toluene (20 mL), washed sequentially with 1M NaOH (20mL), brine (20mL), and distilled H_2O (20 mL). The organic layer was subsequently dried over $MgSO_4$ and concentrated under reduced pressure. After purification by flash column chromatography (20% ethyl acetate in hexanes), the final product was isolated as red crystals in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 8.08 (d, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.40 (m, 2H), 7.22 (t, J = 7.7, 1H), 6.78 (d, J = 7.2 Hz, 1H), 4.01 (bs, 2H), 1.60 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 140.9, 136.3, 135.5, 126.1, 125.6, 123.6, 122.7, 118.9, 116.9, 116.8, 80.2, 28.5. IR (neat): 3362 cm^{-1}, 3300 cm^{-1} (N-H stretch, primary amine), 3050 cm^{-1} (C-H, aromatic stretch), 2977 cm^{-1} (C-H stretch, alkane), 1687 cm^{-1} (C=O stretch, amide), 1152 cm^{-1} (C-O stretch).

***tert*-butyl (8-(dimethylamino)naphthalen-1-yl)carbamate (108):**

To a 100 mL round bottom flask containing **107** (100 mg, 0.38 mmol), was added Na_2CO_3 (210 mg, 2.51 mmol), fitted with a reflux condenser, flame-dried, and backfilled with $N_{2(g)}$. Acetonitrile (10 mL) was then added, followed by the drop-wise addition of freshly distilled Me_2SO_4 (0.26 mL, 2.69 mmol). The reaction mixture was heated to reflux, and stirred for 16 hours. The mixture was then concentrated under reduced pressure, diluted with 20 mL of H_2O, and extracted three times with 10 mL of dichloromethane. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purified compound could be acquired by flash column chromatography (12.5% ethyl acetate in hexanes). The final product was isolated as a clear oil in 70% yield (3.4 mmol, 0.98 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.79 (s, 1H), 8.34 (dd, J = 7.0, 2.3 Hz, 1H), 7.62 (d, J = 8 Hz, 1H), 7.45–7.27 (m, 4H), 2.81 (s, 6H), 1.58 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 150.3, 137.0, 136.1, 126.4, 125.3, 122.0, 119.3, 117.6, 114.1, 79.2, 45.9, 28.5. IR (neat): 3050 cm^{-1} (C-H, aromatic stretch), 2973 cm^{-1}, 2932 cm^{-1}, 2873 cm^{-1}, (C-H stretch, alkane), 1709 cm^{-1} (N-H bend), 1638 cm^{-1} (C=O stretch, amide) 1135 cm^{-1} (C-O stretch). HRMS (ESI): m/z calcd for $C_{17}H_{22}N_2O_2$ ([M+H]+): 287.1754, found: 287.1748.

***N^1,N^1*-dimethylnaphthalene-1,8-diamine (109):**

To a 50 mL round bottom flask containing **108** (250 mg, 0.873 mmol), backfilled with $N_{2(g)}$, was added DCM (15 mL). Trifluoroacetic acid (0.67 mL, 8.73 mmol) was added drop-wise to the resulting mixture and the reaction was allowed to stir for 16 hours at room temperature. The crude product was diluted with 10 mL of H_2O, neutralized with

1M NaOH and extracted three times with 10 mL of dichloromethane. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purified compound could be acquired by flash chromatography (11% ethyl acetate in hexanes). The final product was obtained as a brown oil in a 90% yield (0.830 mmol, 154.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.2 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 6.64 (dd,J= 7.4, 1.1, 1H), 6.18 (bs, 2H). ^{13}C NMR (75 MHz, CDCl3): δ = 152.1, 145.5, 137.0, 126.6, 125.4, 125.4, 118.7, 117.0, 115.1, 109.7, 46.2. IR (neat): 3446 cm^{-1}, 3276 cm^{-1} (N-H stretch, primary amine), 3050 cm^{-1} (C-H, aromatic stretch), 2938 cm^{-1}, 2828 cm^{-1}, 2784 cm^{-1} (C-H stretch, alkane), 1590 cm^{-1} (N-H bend). HRMS (ESI): m/z calcd for $C_{12}H_{14}N_2$ ([M+H]+): 187.1230, found: 186.1239.

***N*-(2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)-8-(dimethylamino)naphthalen-1-aminium chloride (Janus•HCl) (102):**

To a solution of tetrachlorocyclopropene, **52** (0.025 mL, 0.2 mmol), in dichloromethane (2 mL) was added freshly distilled diisopropylamine (0.11 mL, 0.8 mmol) drop-wise under an inert nitrogen atmosphere. The reaction was stirred for four hours at room temperature, after which **109** (16 mg, 0.1 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (11% methanol in DCM) to afford **102** as an off-white solid in 90%

yield (59 mg, 0.08 mmol). m.p. = 225°C–230°C. Subsequent X-ray quality single crystals were grown from benzene and ethyl acetate (see below). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.81 (s, 1H), 7.57–7.54 (m, 1H), 7.41-7.32 (m, 2H), 7.29–7.22 (m, 2H), 6.81 (d, J = 7.0 Hz, 1H), 3.88–3.79 (m, 4H), 2.66 (s, 6H), 1.24 (d, J = 6.8 Hz, 24H). ^{13}C NMR (75 MHz, CDCl3): δ = 150.3, 138.2, 136.2, 126.9, 126.7, 125.3, 123.2, 119.9, 119.4, 118.9, 112.3, 110.0, 51.4, 46.4, 22.1. IR (neat): 3050 cm^{-1} (C-H, aromatic stretch), 2965 cm^{-1}, 2788 cm^{-1} (C-H stretch, alkane), 1709 cm^{-1} (N-H bend), 1524 cm^{-1} (C=C stretch, aromatic), 1489 cm^{-1} (C-N stretch). HRMS (ESI): m/z calcd for $C_{27}H_{40}N_4$ (M+): 421.3326, found: 421.3331

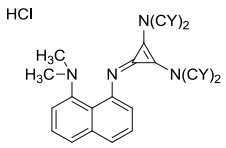
X-ray quality crystals were obtained as follows: Needle-like crystals of **102** were dissolved in vial using slightly more than the minimal amount of benzene required for dissolution. The vial was then placed in a beaker filled half an inch deep with ethyl acetate. The beaker was then capped with aluminum foil and placed in a 5 °C fridge, unperturbed for 72 hours.

N^1-(2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)-N^8,N^8-dimethylnaphthalene-1,8-diamine (Free base of Janus) (95):

Synthesis of 1,8-bis(bis(diisopropylamino)cyclopropeniminenaphthalene, **95**: To a suspension of **102** (35 mg, 0.05 mmol) in toluene (2 mL) under an inert atmosphere, was added dry potassium bis(trimethylsilyl)amide (KHMDS, 0.5M in toluene (0.5 mL, 0.25 mmol), drop-wise. The reaction was stirred for two hours. The volatile components were removed under reduced pressure, and the product was extracted with hot hexane. The resulting product was isolated as yellow crystals in ca. 92% yield (25 mg, 0.04 mmol).

m.p. = 94°C–95°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.37 (dd, J = 8.1, 1.1 Hz, 1H), 7.30 – 7.19 (m,3H), 7.03–7.00 (m, 1H), 6.88 (dd, J = 7.6, 1.2 Hz, 1H) 3.51–3.38 (m, 4H) 2.75 (s, 6H), 1.14 (d, J = 6.8 Hz, 24H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 152.4, 137.7, 125.6, 124.7, 122.5, 120.7, 120.1, 112.8, 112.1, 49.0, 45.5, 22.1. IR (neat): 2965 cm^{-1}, 2925 cm^{-1} (C-H stretch, aromatic), 2818 cm^{-1}, 2765 cm^{-1} (C-H stretch, alkane), 1895 cm^{-1} (N-H bend), 1525 cm^{-1} (C=C stretch, aromatic), 1431 cm^{-1} (C-N stretch). HRMS (ESI): m/z calcd for $C_{27}H_{40}N_4$ (M+): 420.3326, found: 420.3329.

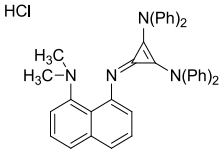
N1-(2,3-bis(dicyclohexylamino)cycloprop-2-en-1-ylidene)-N8,N8-dimethylnaphthalene-1,8-diamine hydrochloride **(111).**



To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added dicyclohexylamine (0.16 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which **109** (37.25 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **111** as a white solid in 82% yield (123.1 mg, 0.18 mmol). m.p. = 125°C - 129°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 13.07 (s, 1H), 7.72 (dd, J = 7.17,

2.17 Hz, 1H), 7.59 (d, J = 7.83 Hz, 1H), 7.47–7.54 (m, 2H), 7.42 (t, J = 7.83 Hz, 1H), 6.94–9.97 (d, J = 7.17, 1H), 3.93–3.47 (m, 1H), 2.82 (s, 6H), 1.84–1.94 (m, 16H), 1.49–1.68 (m, 12H), 1.21–1.34 (m, 8H), 1.03–1.07 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 150.3, 138.0, 136.3, 126.8, 125.7, 123.6, 121.13, 119.3, 118.9, 114.1, 110,5, 60.2, 46.6, 32.4, 25.6, 24.8. HRMS (EI): m/z calcd for $C_{39}H_{56}N_4$ (M+): 580.4505, found: 580.4487

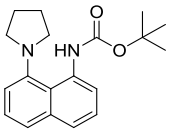
N1-(2,3-bis(diphenylamino)cycloprop-2-en-1-ylidene)-N8,N8-dimethylnaphthalene-1,8-diamine hydrochloride **(112).**



To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diphenylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which **109** (37.3 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **112** as a white solid in 70% yield (83.5 mg, 0.14 mmol). m.p. = 138°C–140°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 15.42 (s, 1H), 6.87–7.95 (m, 26H), 2.95 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.6, 142.8, 137.3, 136.8, 130.0,

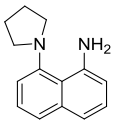
129.6, 129.1, 127.1, 127.0, 125.8, 124.5, 124.1, 124.0, 119.7, 119.0, 116.8, 110.6, 46.34. HRMS (EI): m/z calcd for $C_{39}H_{32}N_4$ (M+): 556.2627, found: 556.2626.

tert-butyl (8-(pyrrolidin-1-yl)naphthalen-1-yl)carbamate **(120).**



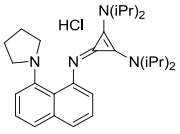
A 50 mL RBF containing **107** (258.3 mg, 1.0 mmol), was fitted with a reflux condenser and backfilled with $N_{2(g)}$. DMF (5mL), followed by 1,4-dibromobutane (0.12 mL, 1.0 mmol), were then added and the reaction heated to 60 °C for 48 hours. The crude reaction mixture diluted with H_2O (15 mL) and extracted three times with 10mL DCM. The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (6 hexane:1 ethyl acetate) to afford **120** as a dark brown oil in 84% yield (262.4 mg, 0.84 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 13.11 (s, 1H), 8.35 (dd, J = 6.79, 2.53 Hz, 1H), 7.63 (dd, 6.78, 2.69 Hz, 1H), 7.34–7.47 (m, 4H), 3.38–3.44 (m, 2H), 2.87–2.93 (m, 2H), 2.00–2.18 (m, 4H), 1.57 (s, 1H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 153.5, 146.3, 137.3, 136.0, 126.4, 125.4, 121.8, 120.2, 118.0, 113.5, 79.1, 54.6, 28.5, 24.0. HRMS (EI): m/z calcd for $C_{19}H_{24}N_2O_2$ (M+): 312.1838, found: 312.2.

8-(pyrrolidin-1-yl)naphthalen-1-amine **(118).**



A 50 mL RBF containing Na_2CO_3 (455 mg, 4.2 mmol), fitted with a reflux condenser, was flame-dried and backfilled with $N_{2(g)}$. A solution of 1,8-diaminonaphthalene, **17** (316.2 mg, 2.0 mmol) in DMF (5 mL) was then added under the inert nitrogen atmosphere, followed by 1,4-dibromobutane (0.24 mL, 2.0 mmol). The reaction was heated to 60 °C for 48 hours. The crude reaction mixture was partitioned between H_2O (15 mL) and DCM (15 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (6 hexane:1 ethyl acetate) to afford **118** as a dark brown oil in 24% yield (101.9 mg, 0.48 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.52 (dd, J = 9.1, 1.10 Hz, 1H), 7.14–7.34 (m, 4H), 6.62 (dd, J = 7.37, 1.17 Hz, 1H), 6.15 (bs, 2H), 3.45–3.49 (m, 2H), 2.80–2.87 (m, 2H), 2.00–2.04 (m, 4H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 148.5, 137.9, 136.0, 127.1, 126.7, 125.2, 123.9, 121.0, 120.4, 120.2, 119.9, 113.4, 110.6, 56.6, 51.5, 25.0, 22.3. HRMS (EI): m/z calcd for $C_{14}H_{16}N_2$ (M+): 212.1314, found: 212.1309.

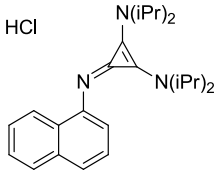
N1,N1,N2,N2-tetraisopropyl-3-((8-(pyrrolidin-1-yl)naphthalen-1-yl)imino)cycloprop-1-ene-1,2-diamine hydrochloride **(113).**



To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8

mmol). The reaction was stirred for four hours at room temperature, after which **118** (42.5 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography in (11% methanol in DCM) to afford **113** as a white solid in 91% yield (88.5 mg, 0.18 mmol). m.p. = 72°C–78°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 13.42 (s, 1H), 7.68 (dd, J = 7.32, 2.10 Hz, 1H), 7.43–7.54 (m, 3H), 7.38 (t, J = 7.51 Hz, 1H), 6.87 (dd, J = 7.35, 1.00 Hz, 1H), 3.86–3.99 (m, 4H), 3.38 (bs, 2H), 3.08 (bs, 2H), 2.14 (bs, 2H), 1.97 (bs, 2H), 1.35 (d, J = 6.78 Hz, 24H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ =148.5, 137.9, 136.0, 127.1, 125.2, 123.9, 120.4, 120.2, 119.9, 113.4, 110.6, 56.6, 51.5, 25.0, 22.3. HRMS (EI): m/z calcd for $C_{29}H_{42}N_4$ (M+): 447.3482, found: 447.3490.

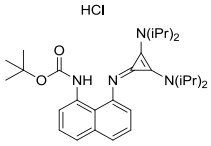
N1,N1,N2,N2-tetraisopropyl-3-(naphthalen-1-ylimino)cycloprop-1-ene-1,2-diamine hydrochloride (114).



To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which 1-naphthylamine (28.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The

crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **113** as a white solid in 95% yield (21.7 mg, 0.19 mmol). m.p. = 250°C–255°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.58 (s, 1H), 7.98 (dd, J = 6.22, 1.08 Hz, 1H), 7.80–7.83 (m, 1H), 7.72 (d, 8.32 Hz, 1H), 7.59 (d, J = 7.14 Hz, 1H), 7.37–752 (m, 3H) 3.42–3.56 (m, 4H), 1.13 (d, J = 6.89 Hz, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 152.8, 134.7, 130.5, 127.3, 125.9, 125.2, 125.1, 124.7, 123.8, 118.6, 116.4, 113.7, 49.4, 22.3. HRMS (EI): m/z calcd for $C_{25}H_{35}N_3$ (M+): 377.2831, found: 377.2822.

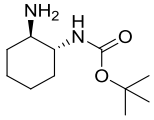
tert-butyl (8-((2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)amino)naphthalen-1-yl)carbamate hydrochloride **(115).**



To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which **108** (57.3 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under

reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) o afford **115** as a light red solid in 90% yield (95.2 mg, 0.18 mmol). The solid decomposes before reaching its melting point. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.57 (s, 1H), 9.22 (s, 1H), 7.81 (dd, J = 7.82, 1.34 Hz, 1H), 7.72 (d, J = 7.94 Hz, 1H), 7.65 (d, J = 7.26 Hz, 1H), 7.48 (t, J = 7.89 Hz, 1H), 7.33–7.42 (m, 2H), 3.52–3.65 (m, 4H), 1.48 (s, 9H), 1.24 (d, J = 6.93 Hz, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.1, 136.2, 134.9, 133.1, 129.2, 127.6, 127.3, 126.7, 126.6, 126.3, 124.7, 115.6, 114.0, 79.0, 50.7, 28.5, 22.0. HRMS (EI): m/z calcd for $C_{30}H_{44}N_4O_2$ (M+): 492.3464, found: 492.3448.

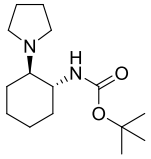
tert-butyl (trans)-2-aminocyclohexyl)carbamate (**122**)[160]



To a 50 mL RBF, flame-dried and backfilled with $N_{2(g)}$, was added 1,2-*trans*-diaminocyclohexane (0.48 mL, 4.0 mmol), and 10 mL DCM. The reaction was cooled to 0 °C in an ice bath, and a solution of di-*tert*-butyl dicarbonate (Boc_2O, 436.5 mg, 2.0 mmol) in DCM (8 mL) was added over two hours *via* syringe pump. The reaction was stirred for an additional 3 hours at room temperature. The reaction mixture was diluted with H_2O (10 mL) acidified to pH 5 with 1M HCl and the organic layer extracted with Et_2O (10 mL). The aqueous layer was then basified to pH 10 with 1M NaOH and

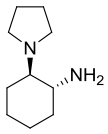
extracted three times with 10mL EtOAc. The combined EtOAc extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The product was obtained in sufficiently pure form as a white solid in 35% yield (300.0 mg, 1.4 mmol). m.p. = 113–115 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.67 (bs, 1H), 3.02–3.12 (m, 1H), 2.33–2.31 (m, 1H), 1.88–1.97 (m, 2H), 1.65 (dt, J = 9.63, 2.69 Hz, 2H), 1.40 (s, 9H), 1.04–1.31 (m, 6H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 157.4, 78.9, 57.1, 54.4, 33.9, 32.6, 27.9, 25.3, 25.1.

tert-butyl (trans)-2-(pyrrolidin-1-yl)cyclohexyl)carbamate **(123)**



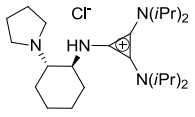
A 50 mL RBF containing Na_2CO_3 (296.8 mg, 2.8 mmol), fitted with a reflux condenser, was flame-dried and backfilled with $N_{2(g)}$. Intermediate **122** (300.0 mg, 1.4 mmol), DMF (5 mL), and 1,4-dibromobutane (0.17 mL, 1.4 mmol) were then added and the reaction was heated to 60 °C for 24 hours. The crude reaction mixture was partitioned between H_2O (15 mL) and DCM (15 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (5% methanol in DCM) to afford **123** as an orange oil in 90% yield (338.14 mg, 1.26 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.22 (bs, 1H), 3.27–2.22 (m, 1H), 2.60–2.64 (m, 2H), 2.50–2.56 (m, 2H), 2.34–2.44 (m, 2H), 1.70–1.79 (m, 6H), 1.45 (s, 9H), 1.10–1.39 (m, 4H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.0, 78.9, 62.3, 52.1, 47.9, 32.2, 28.3, 24.2, 24.0, 23.6, 23.2.HRMS (EI): m/z calcd for $C_{15}H_{28}N_2O_2$ (M+): 268.2151, found: 268.2149.

(trans)-2-(pyrrolidin-1-yl)cyclohexanamine (**124**)



To a 50 mL round bottom flask containing **123** (214.7 mg, 1.12 mmol), backfilled with N_{2g}, was added was added DCM (15 mL), followed by drop-wise addition of trifluoroacetic acid (0.86 mL, 11.2 mmol). The reaction was stirred at room temperature for 16 hours. The crude product was diluted with H_2O (10 mL), basified to pH 10 with 1M NaOH and extracted 3x with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (11% ethyl acetate in hexanes) to afford **124** as a brown oil in a 90% yield (170.0 mg, 1.01 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.32**–**2.66 (m, 4H), 2.26 (m, 1H), 1.95 (m, 1H), 1.69**–**1.97 (m, 8H), 1.33 (m, 4H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 65.2, 52.8, 47.1, 35.0, 25.5, 25.0, 23.8, 21.5. HRMS (EI): m/z calcd for $C_{10}H_{20}N_2$ (M+): 168.1627, found: 168.1620.

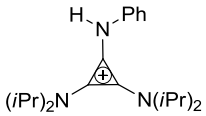
N1-(2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)-N2,N2-dimethylcyclohexane-1,2-diamine hydrochloride **(115).**



To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which **124**

(33.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **116** as a yellow oil in 41% yield (35.1 mg, 0.08 mmol). ^{1}H-NMR (300 MHz, $CO(CD_3)_2$): δ =4.04 (m, 4H), 3.50 (m, 1H), 3.30 (m, 1H), 2.80 (m, 4H), 2.09 (m, 4H), 1.58–1.87 (m, 8H), 1.36 (d, J = 6.82, 24H).^{13}C-NMR (75 MHz, $CO(CD_3)_2$): δ =117.4, 114.7 62.2, 60.3, 50.6, 48.5, 33.7, 24.7, 24.7, 23.3, 21.5, 21.2. HRMS (EI): m/z calcd for $C_{25}H_{47}N_4$ (M+): 403.3795, found: 403.3795.

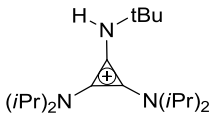
***N-(2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)benzenaminium chloride* (116).[161]**



To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which aniline (18.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by crystallization in MeCN/EtOAc

(1:1) to afford **117** as a white crystalline solid in 96% yield (69.9 mg, 0.19 mmol). m.p. = 188–190 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.69 (s, 1H), 7.41–7.45 (m, 2H), 7.30–7.35 (m, 2H), 7.10–7.15 (m, 1H), 3.75–3.89 (m, 4H), 1.35 (d, J = 6.83 Hz, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.5, 130.0, 126.4, 123.2, 117.1, 112.9, 51.4, 22.2.

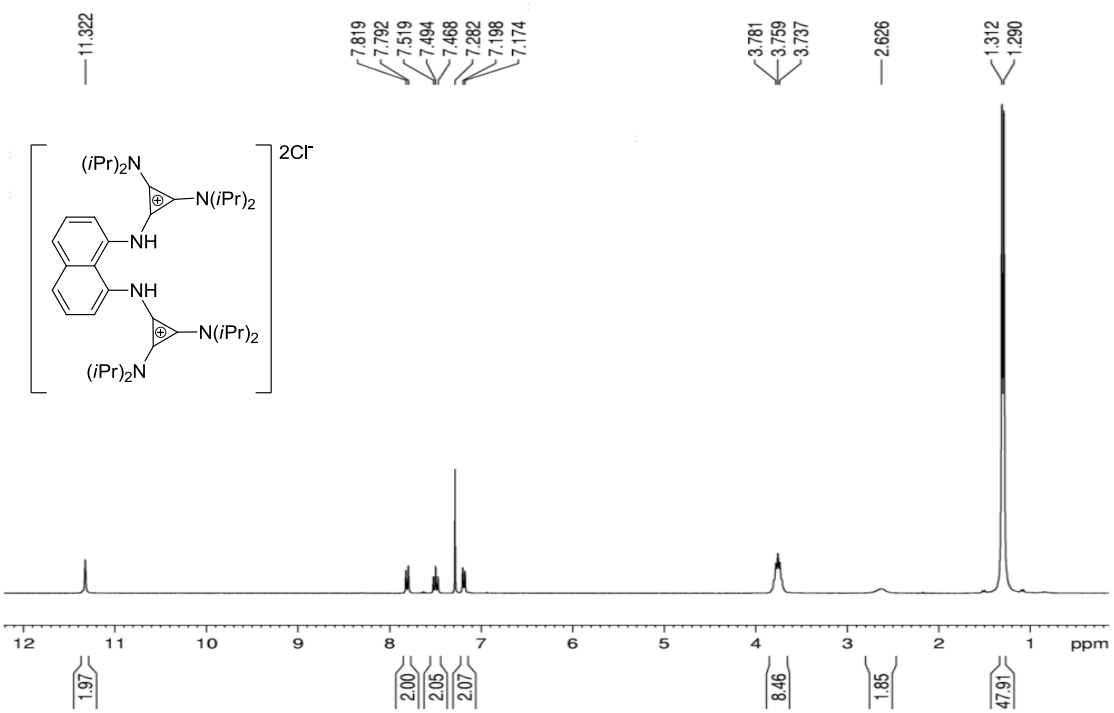
3-(tert-butylimino)-N1,N1,N2,N2-tetraisopropylcycloprop-1-ene-1,2-diamine hydrochloride **(104).**[162]



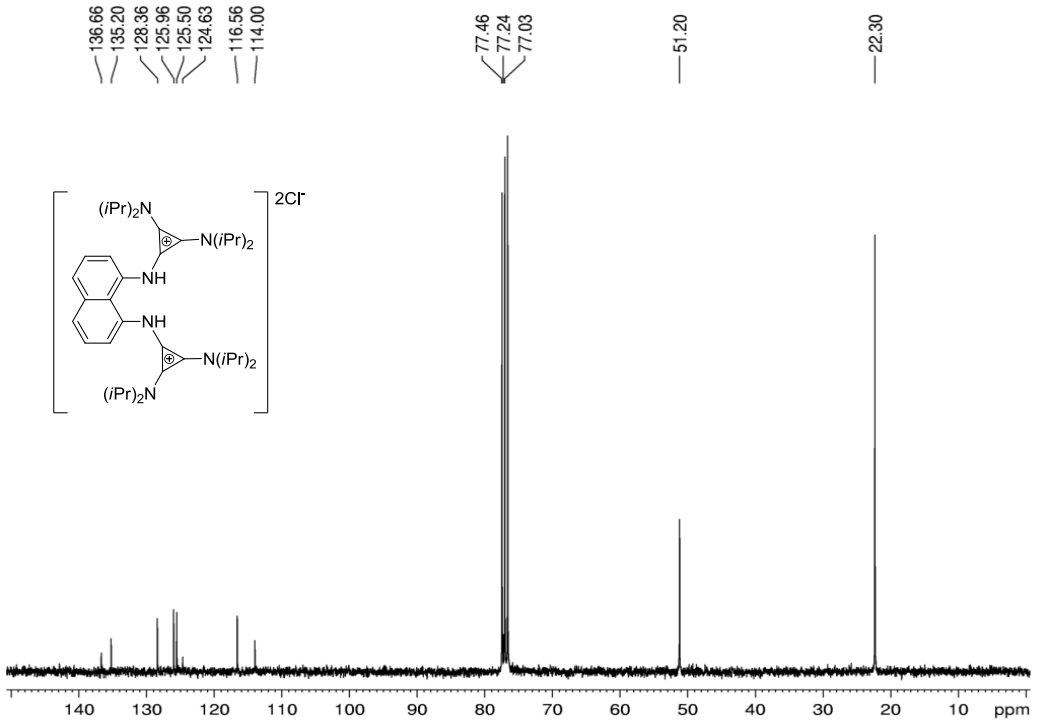
To a solution of tetrachlorocyclopropene, **52** (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *tert*-butylamine (14.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by crystallization in MeCN/EtOAc (1:1) to afford **104** as a white crystalline solid in 98% yield (67.4 mg, 0.2 mmol). m.p. = 171°C–172°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.99–4.08 (m, 4H), 1.49 (s, 9H), 1.35 (d, J = 6.82, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 118.0, 116.8, 53.3, 51.0, 30.3, 22.5.

Spectral Data

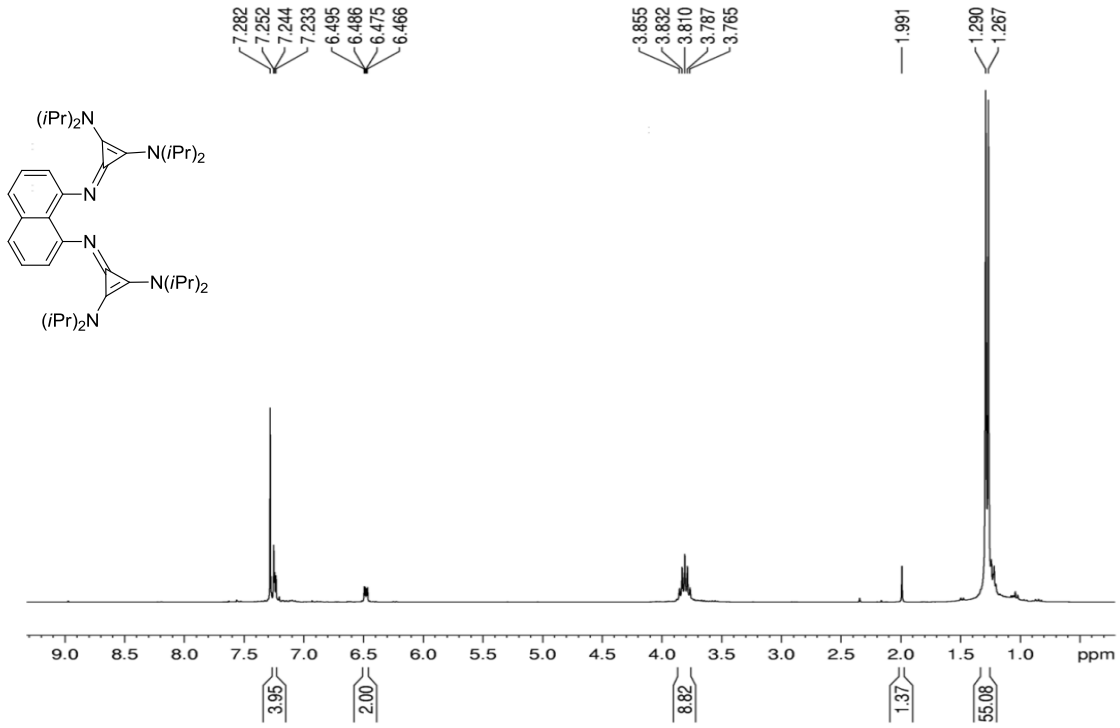
^{1}H NMR spectrum of **90** in $CDCl_3$



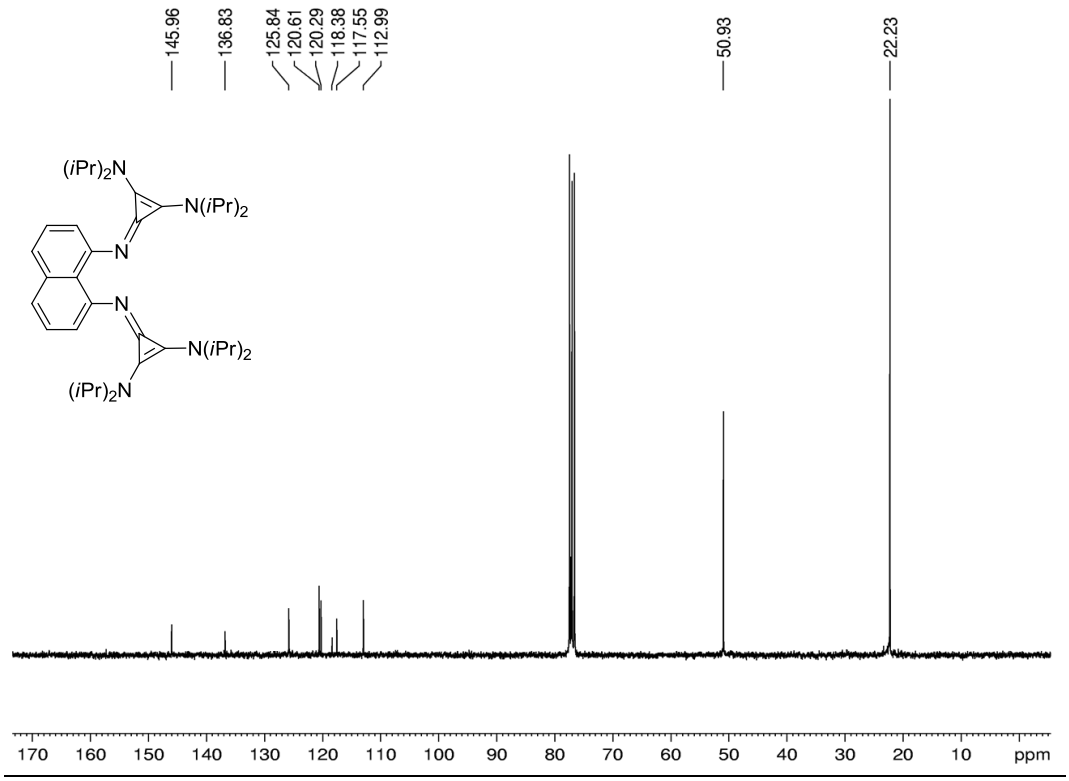
^{13}C NMR spectrum of **90** in $CDCl_3$



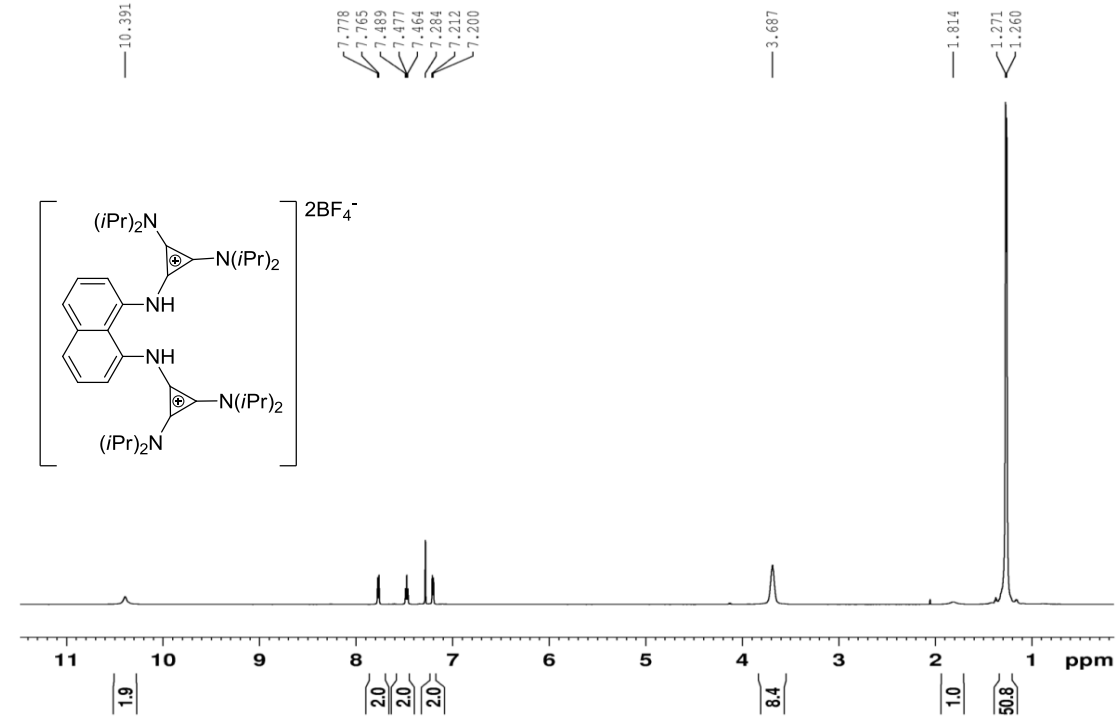
^{1}H NMR spectrum of **89** in $CDCl_3$



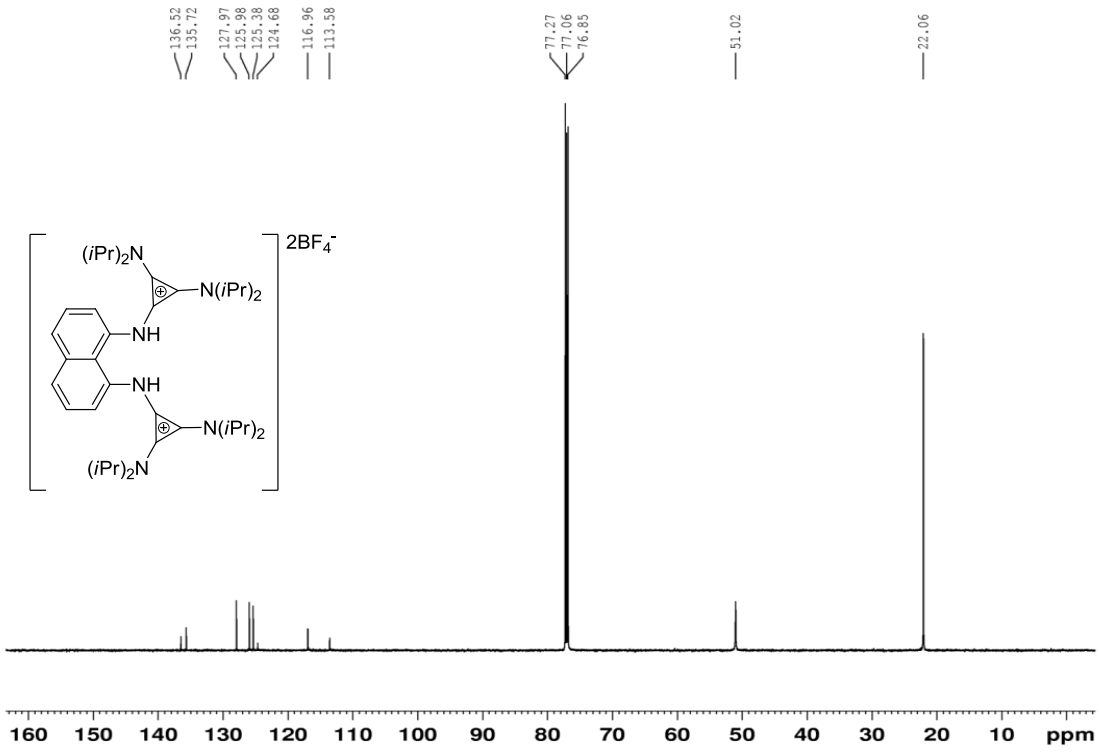
^{13}C NMR spectrum of **89** in $CDCl_3$



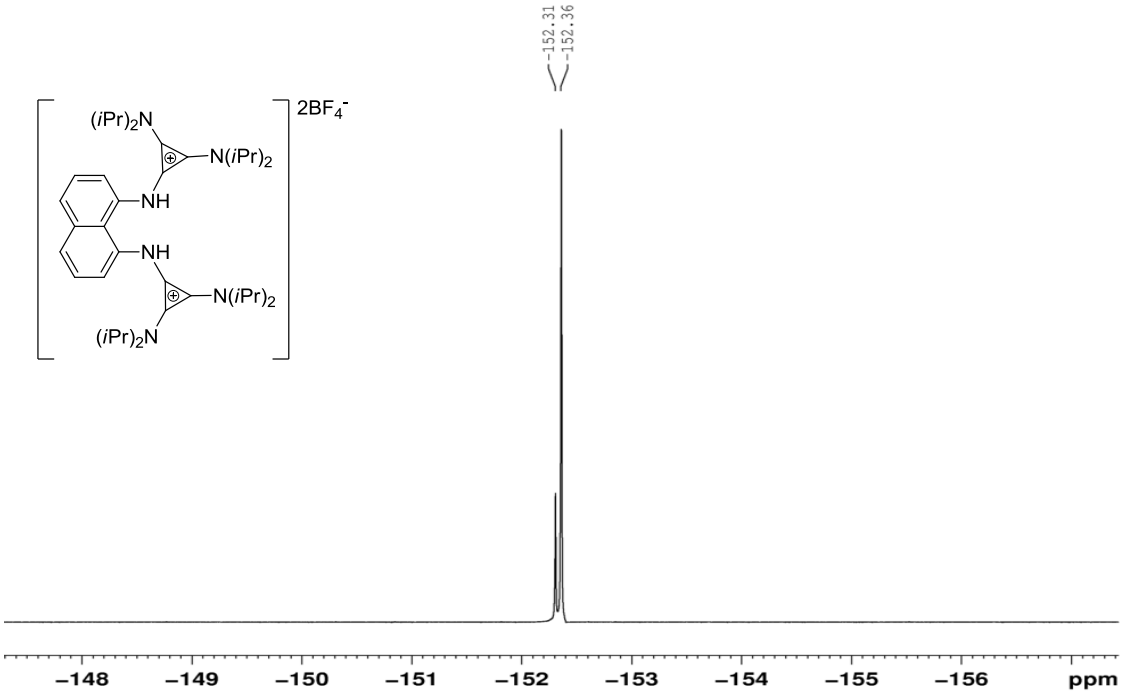
^{1}H NMR spectrum of **90•BF_4** in $CDCl_3$



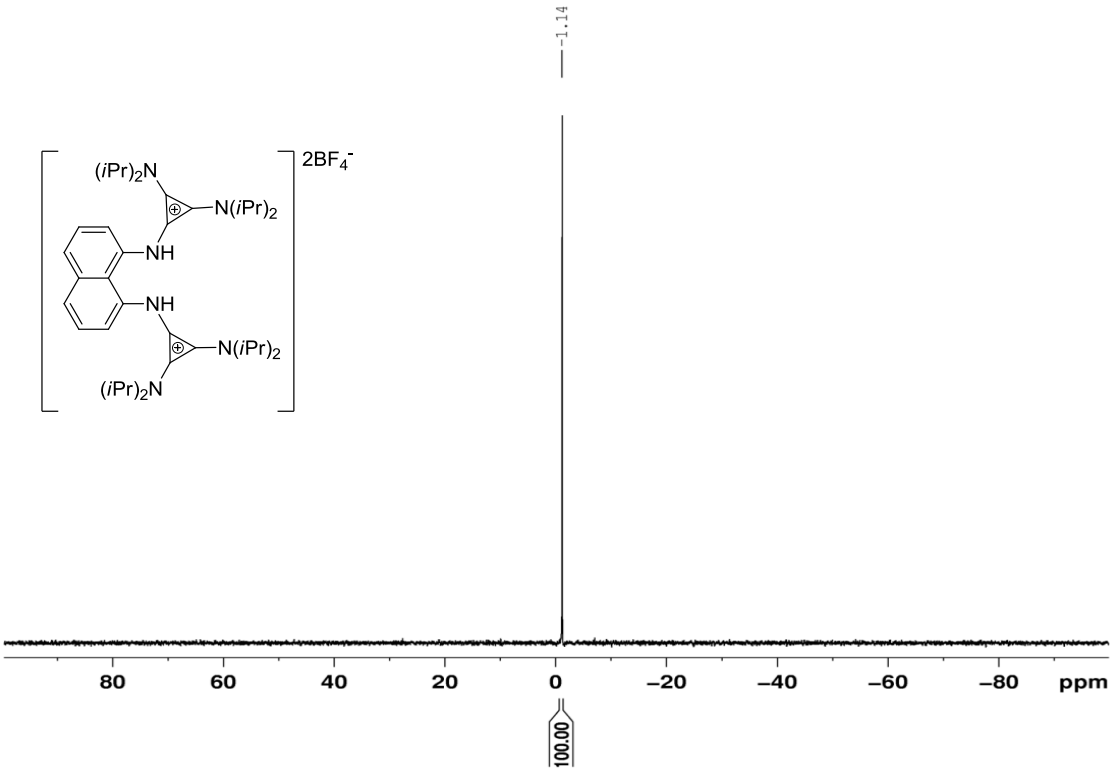
^{13}C NMR spectrum of **90•BF_4** in $CDCl_3$



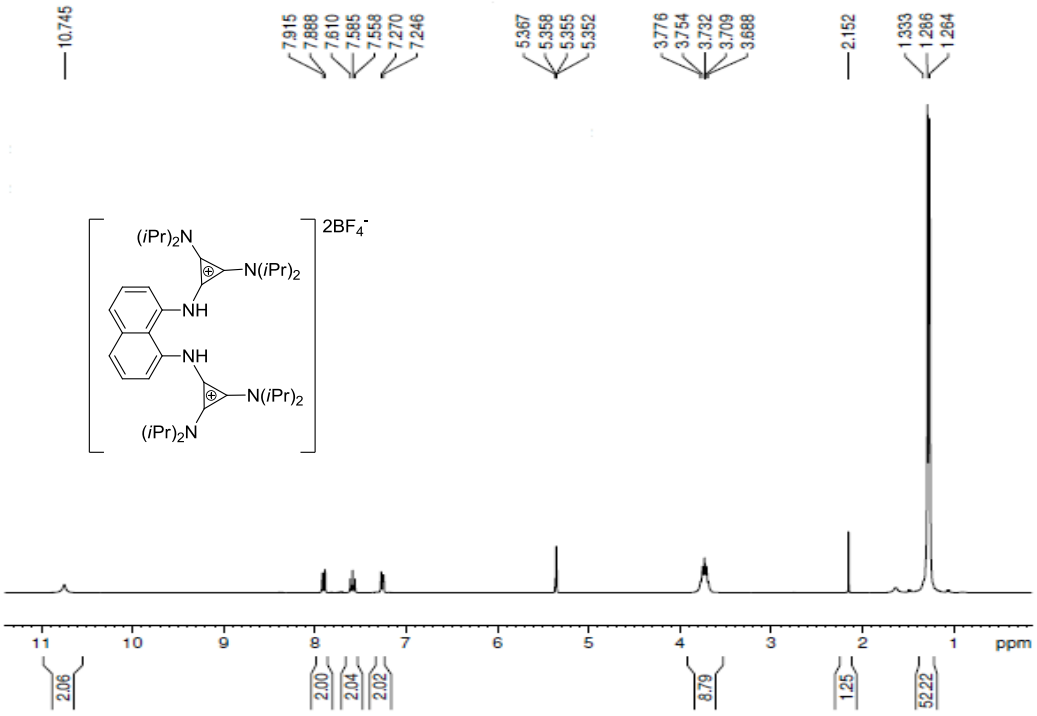
^{19}F NMR spectrum of **90•BF$_4$** in $CDCl_3$



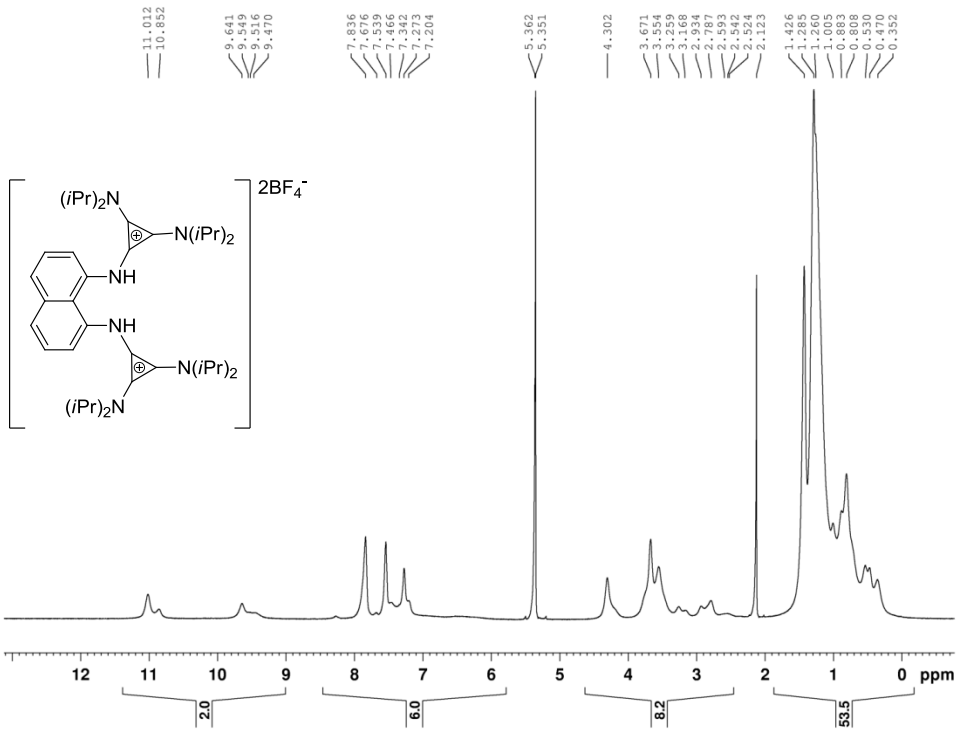
^{11}B NMR spectrum of **90•BF$_4$** in $CDCl_3$



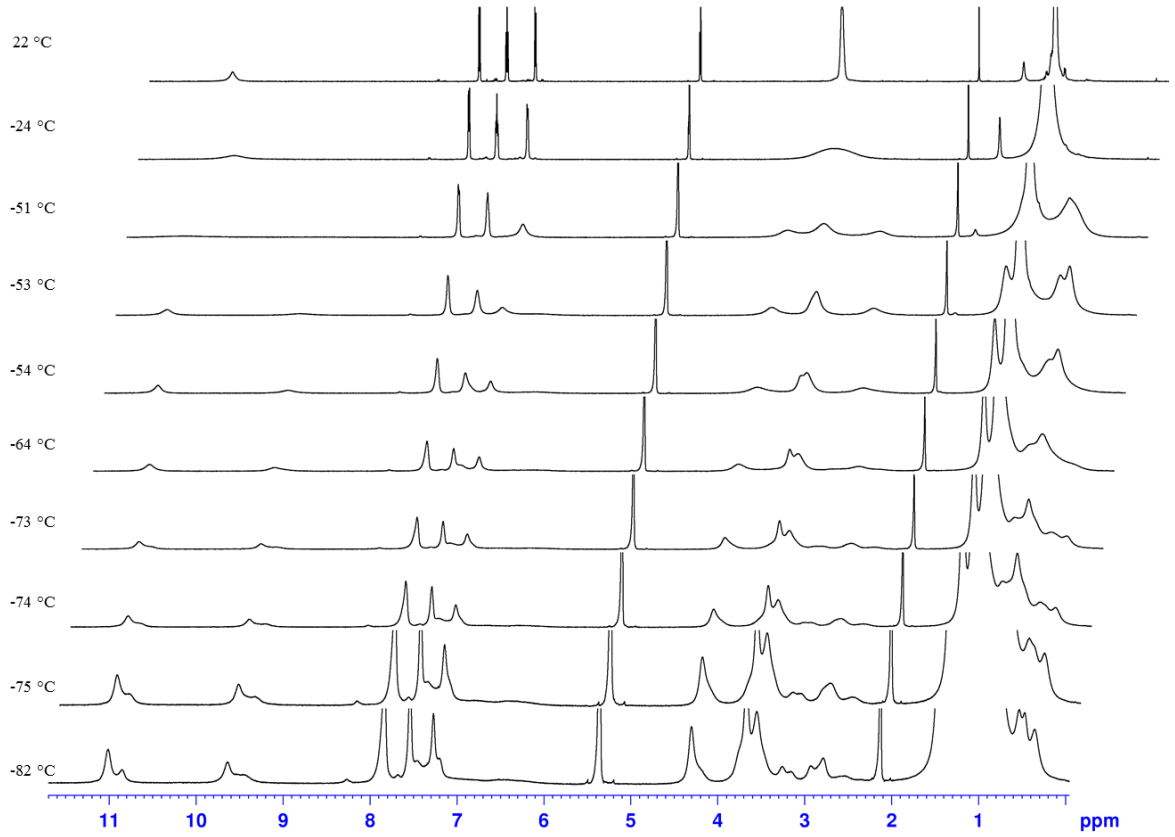
^{1}H NMR spectrum of **90•$(BF_4)_2$** in CD_2Cl_2



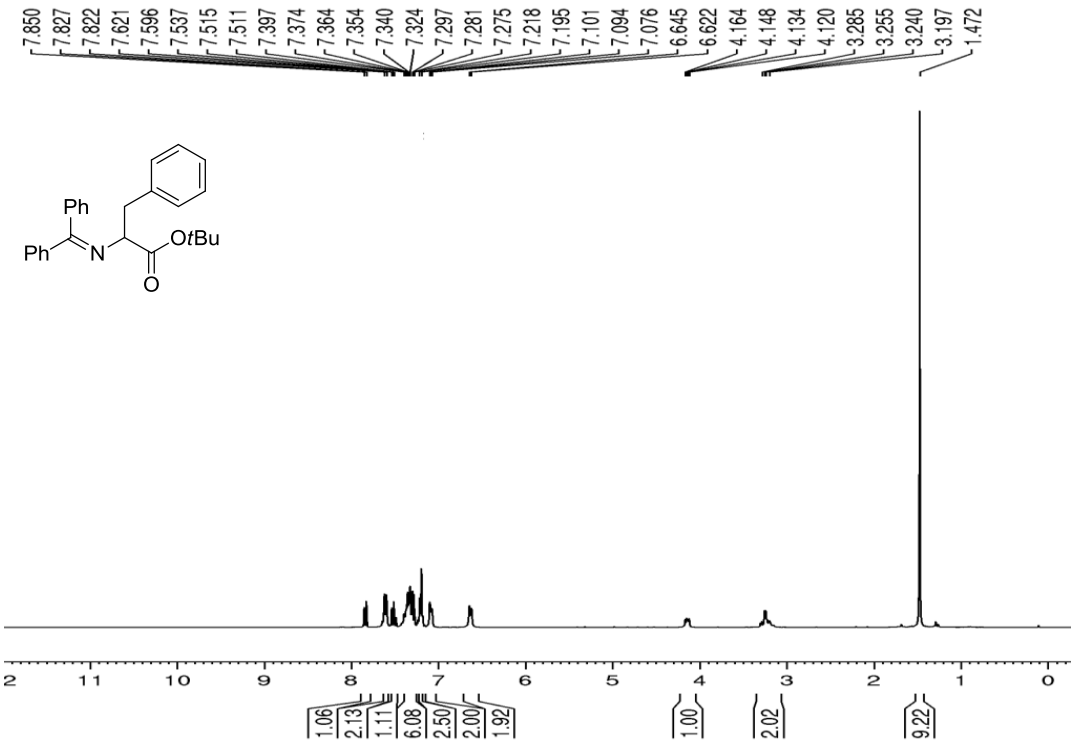
^{1}H NMR spectrum of **90•$(BF_4)_2$** in CD_2Cl_2 at -82 °C



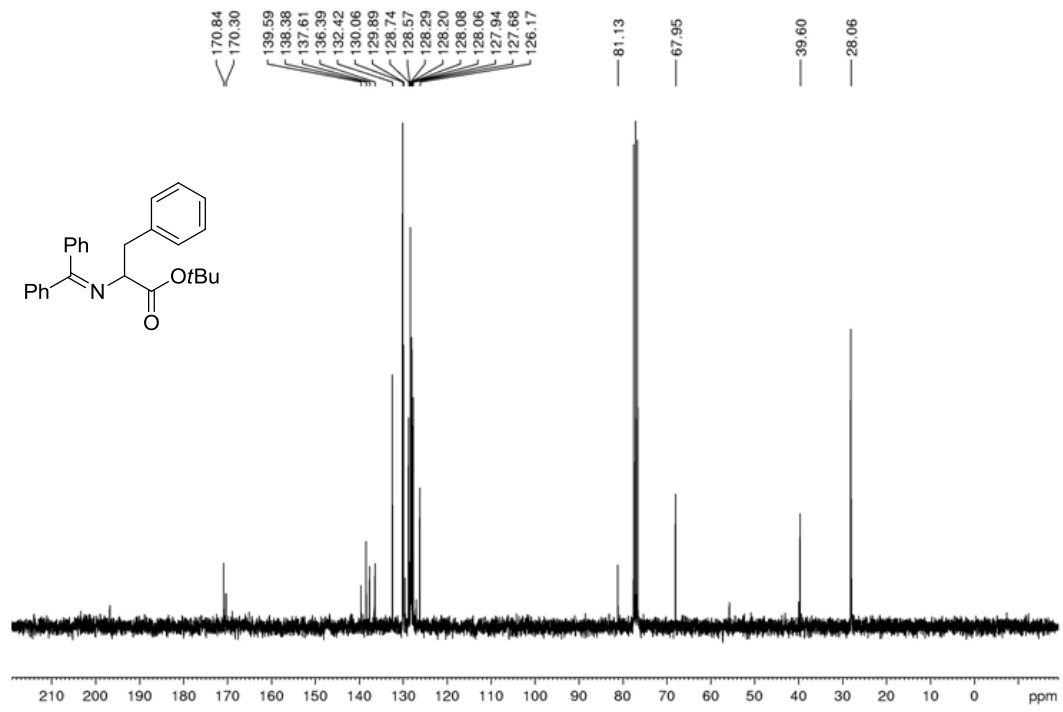
Stacked ^{1}H NMR spectrum of **90•$(BF_4)_2$** in CD_2Cl_2 at -22°C, -24°C, -51°C, -53°C, -54°C, -64°C, -73°C, -74°C, -75°C, and -82 °C.



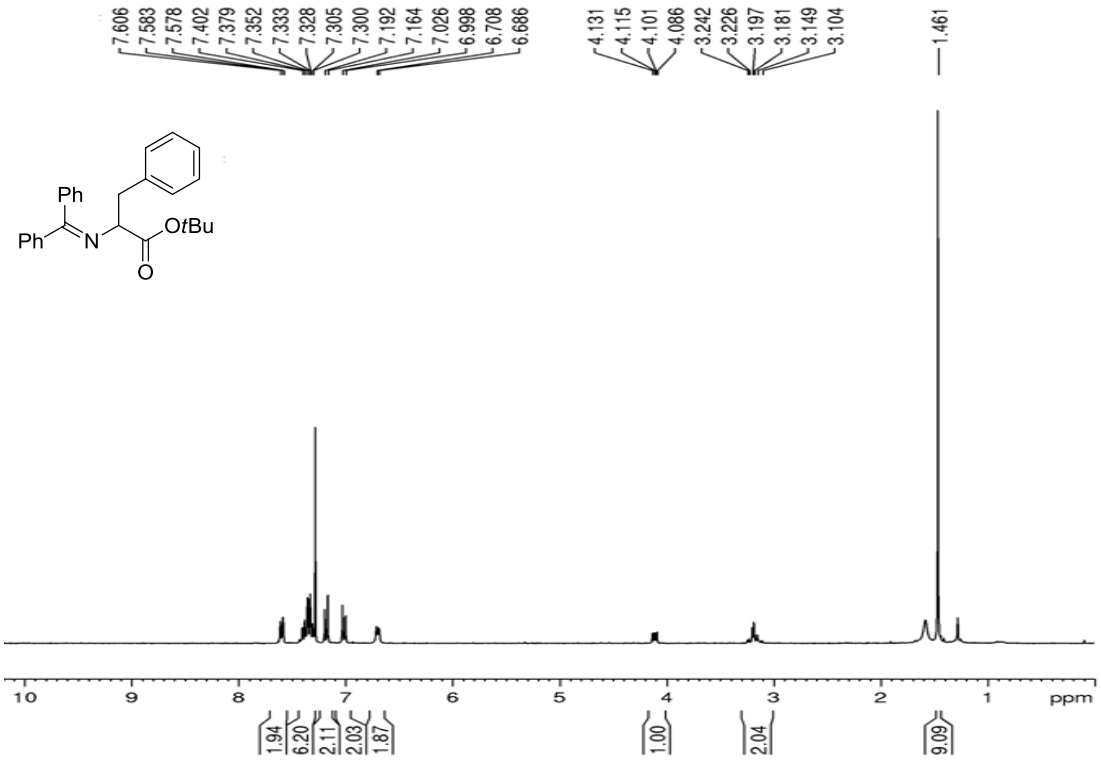
^{1}H NMR spectrum of **101a** in $CDCl_3$



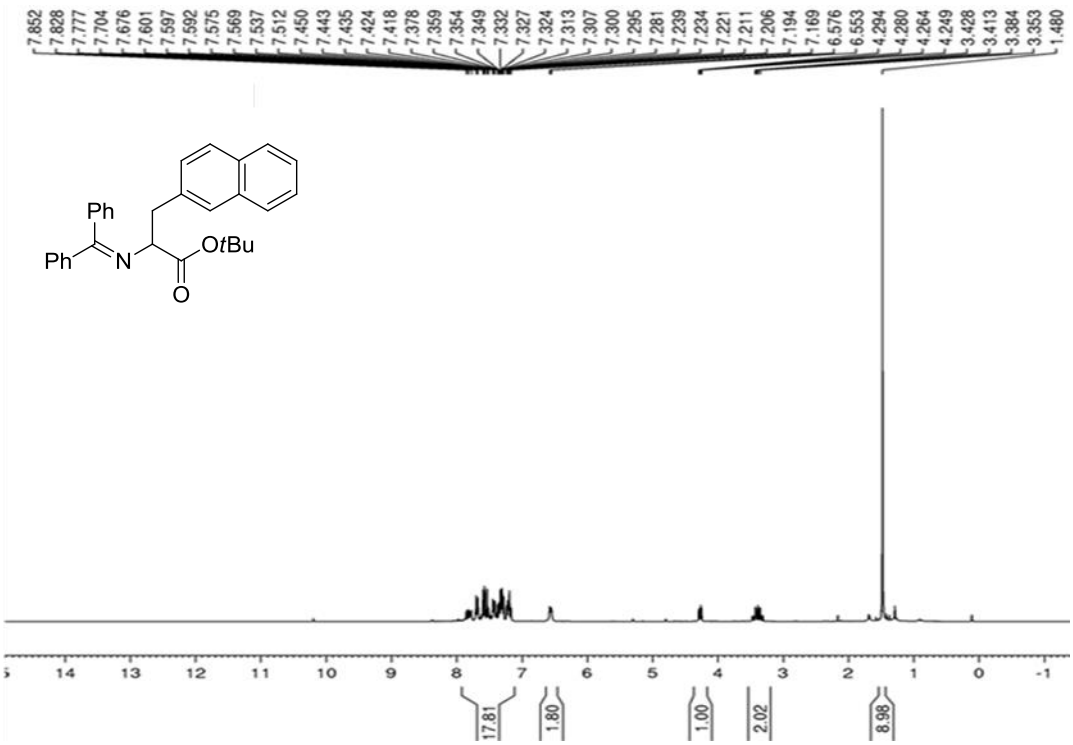
^{13}C NMR spectrum of **101a** in $CDCl_3$



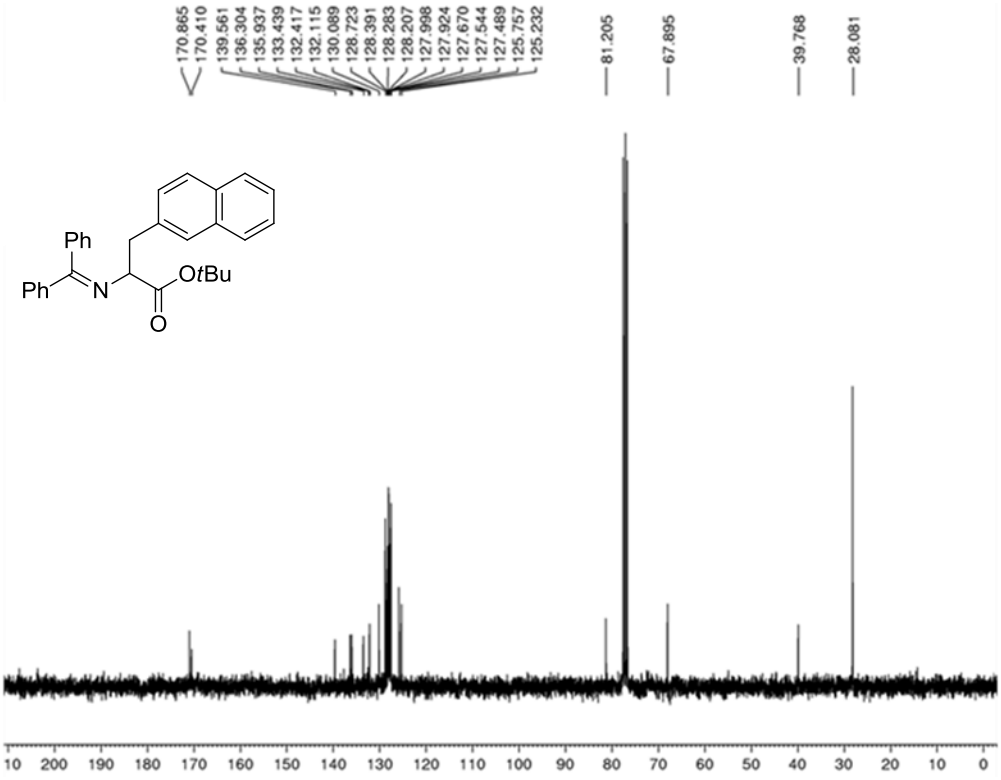
^{1}H NMR spectrum of **101d** in $CDCl_3$



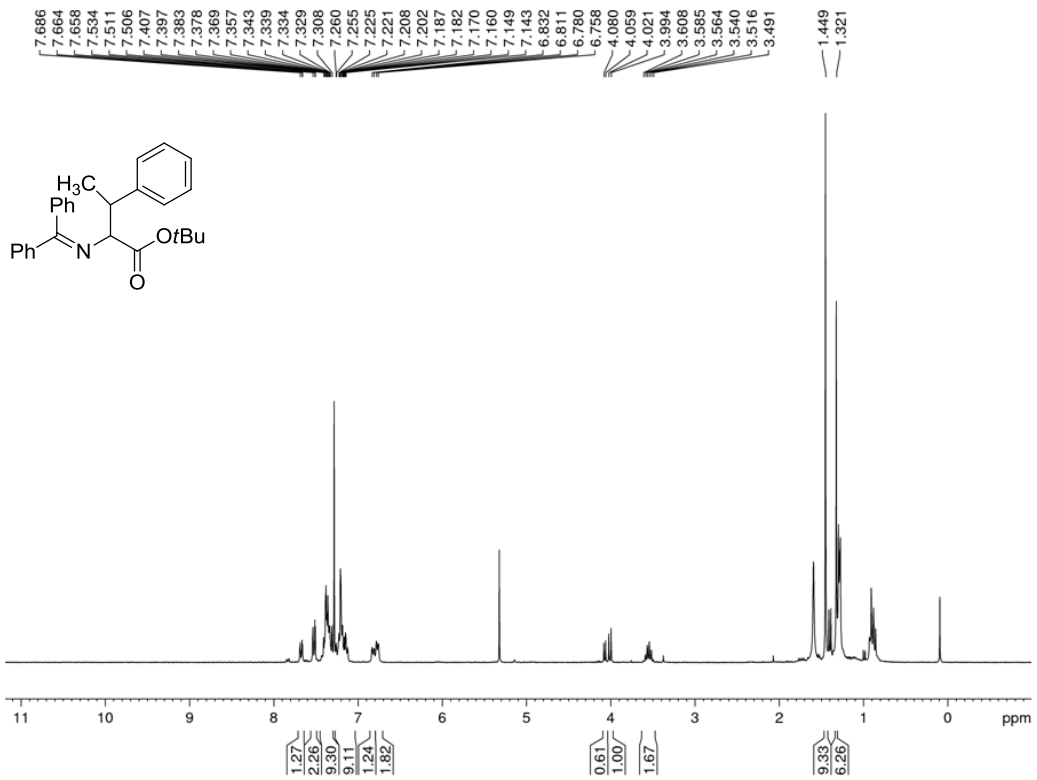
^{1}H NMR spectrum of **101b** in $CDCl_3$



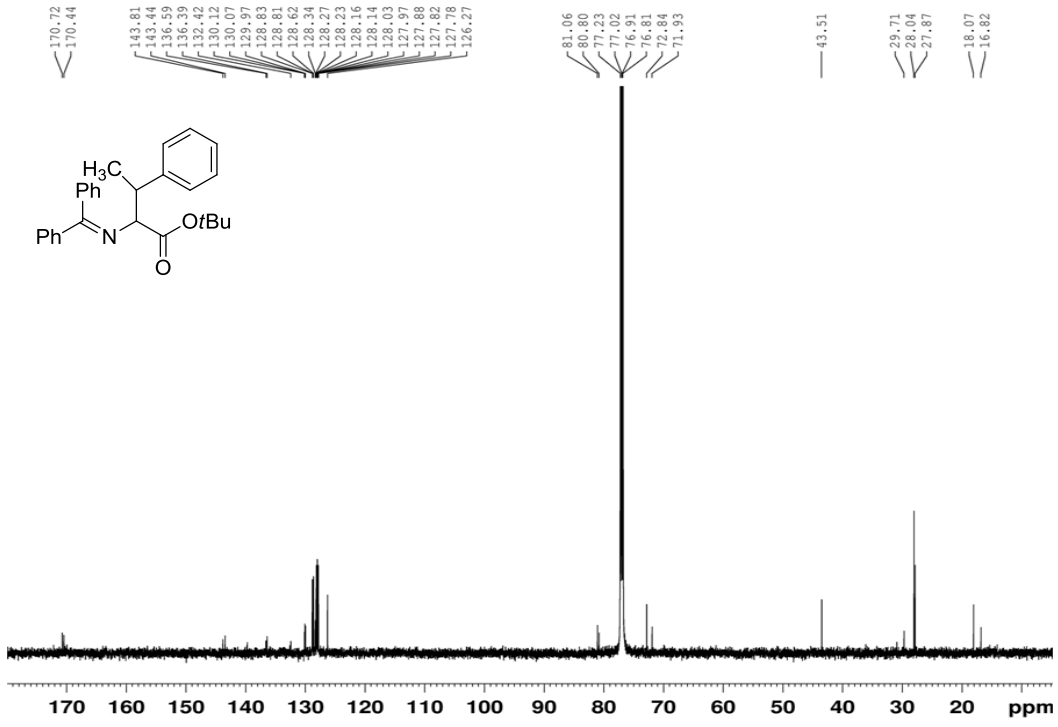
^{13}C NMR spectrum of **101b** in $CDCl_3$



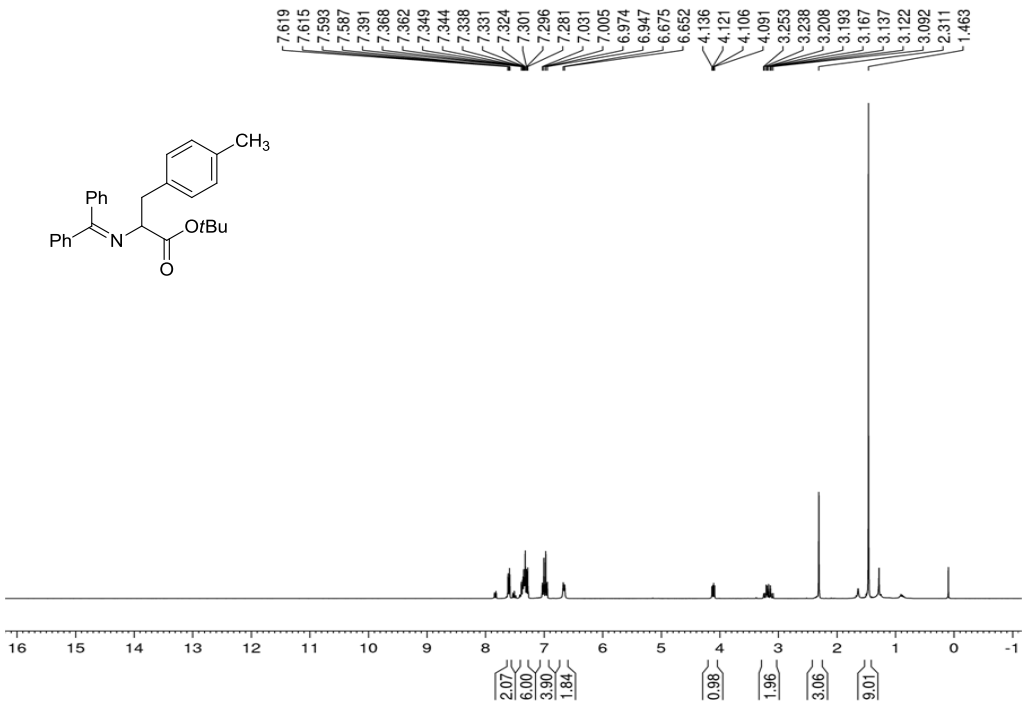
^{1}H NMR spectrum of **101c** in $CDCl_3$



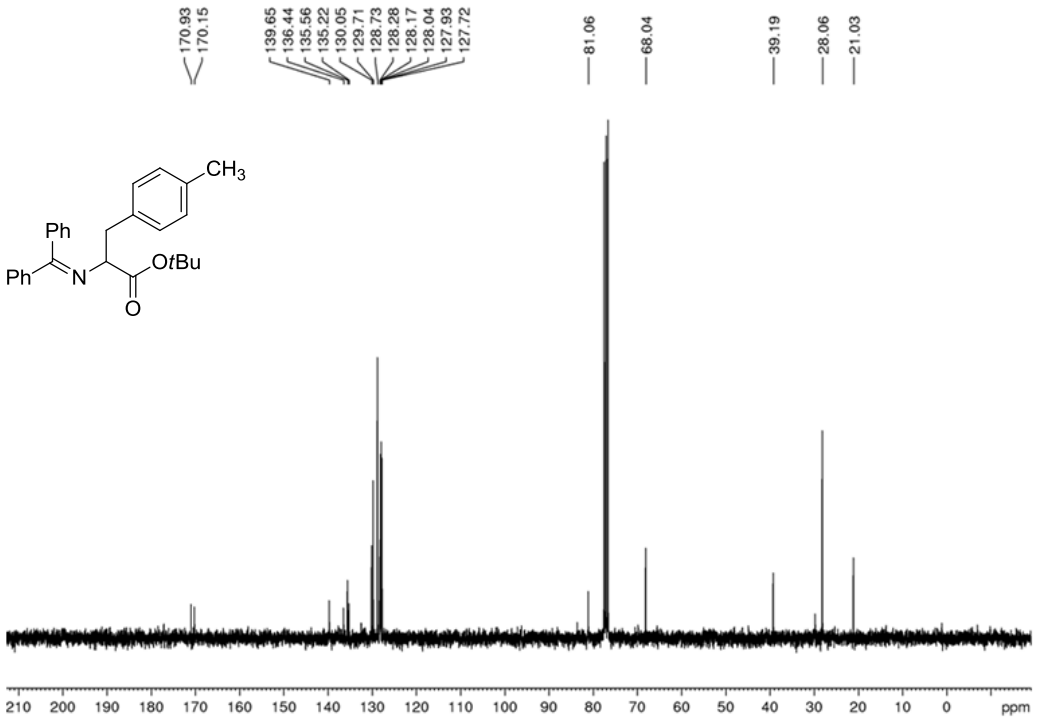
^{13}C NMR spectrum of **101b** in $CDCl_3$



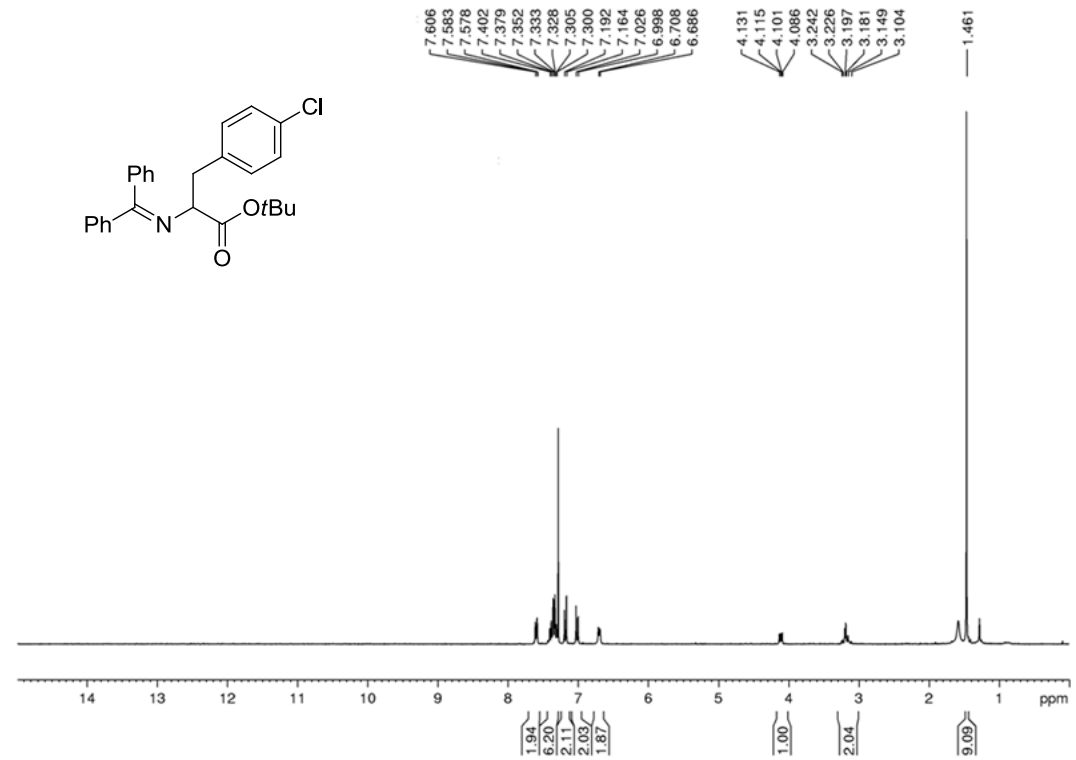
^{1}H NMR spectrum of **101f** in $CDCl_3$



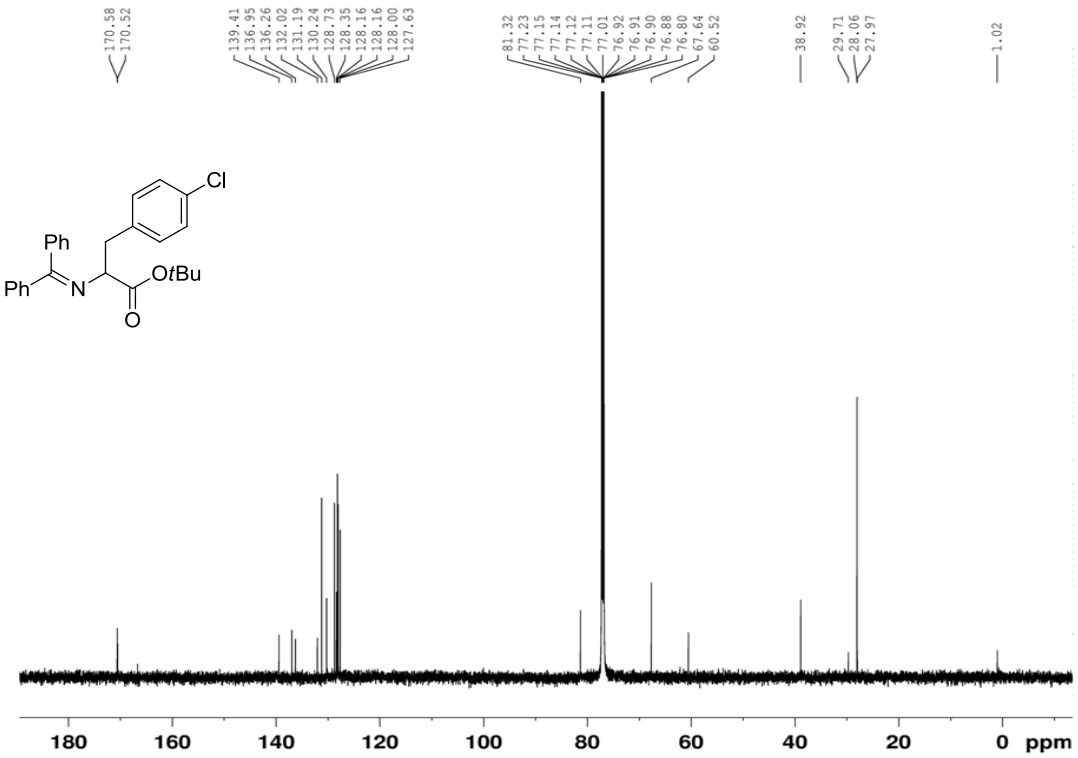
^{13}C NMR spectrum of **101f** in $CDCl_3$



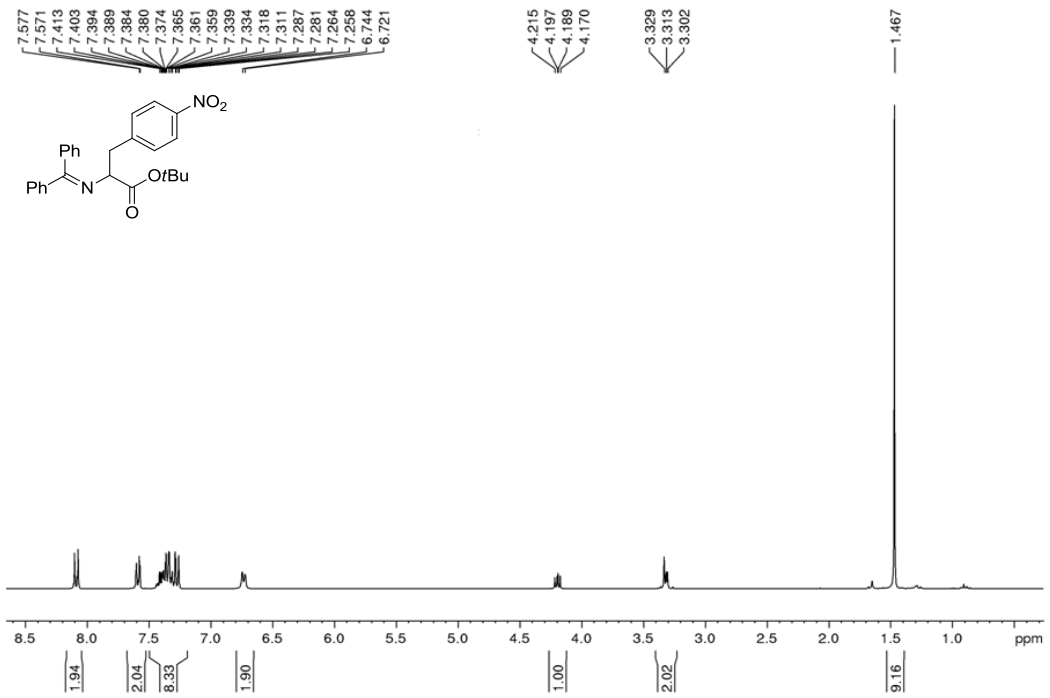
^{1}H NMR spectrum of **101g** in $CDCl_3$



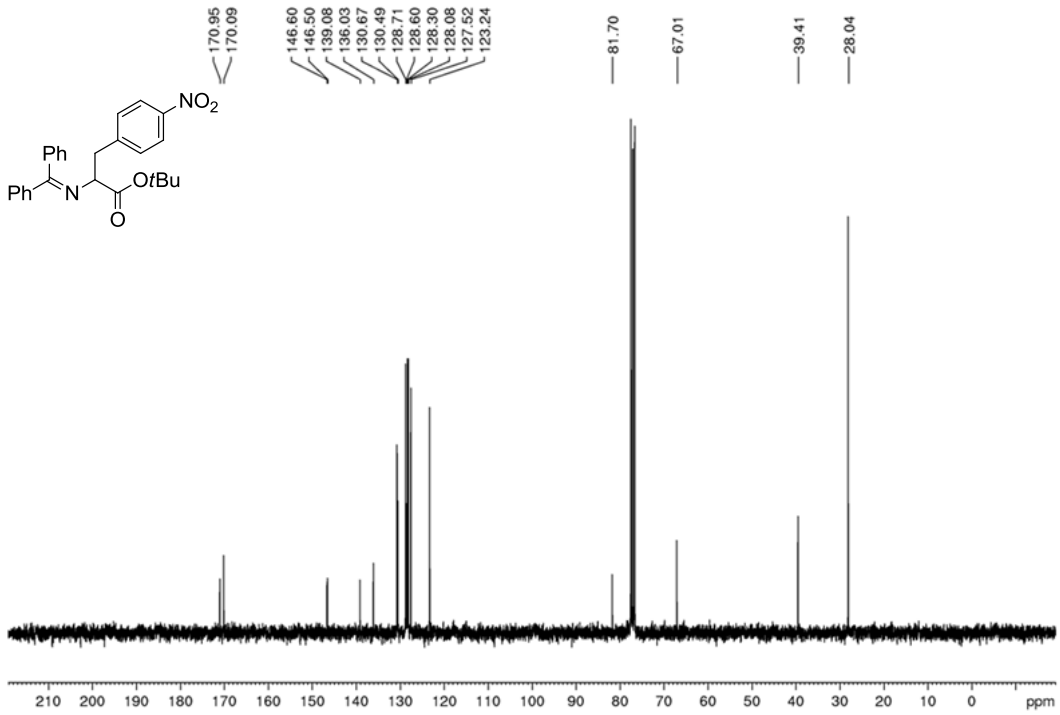
^{13}C NMR spectrum of **101g** in $CDCl_3$



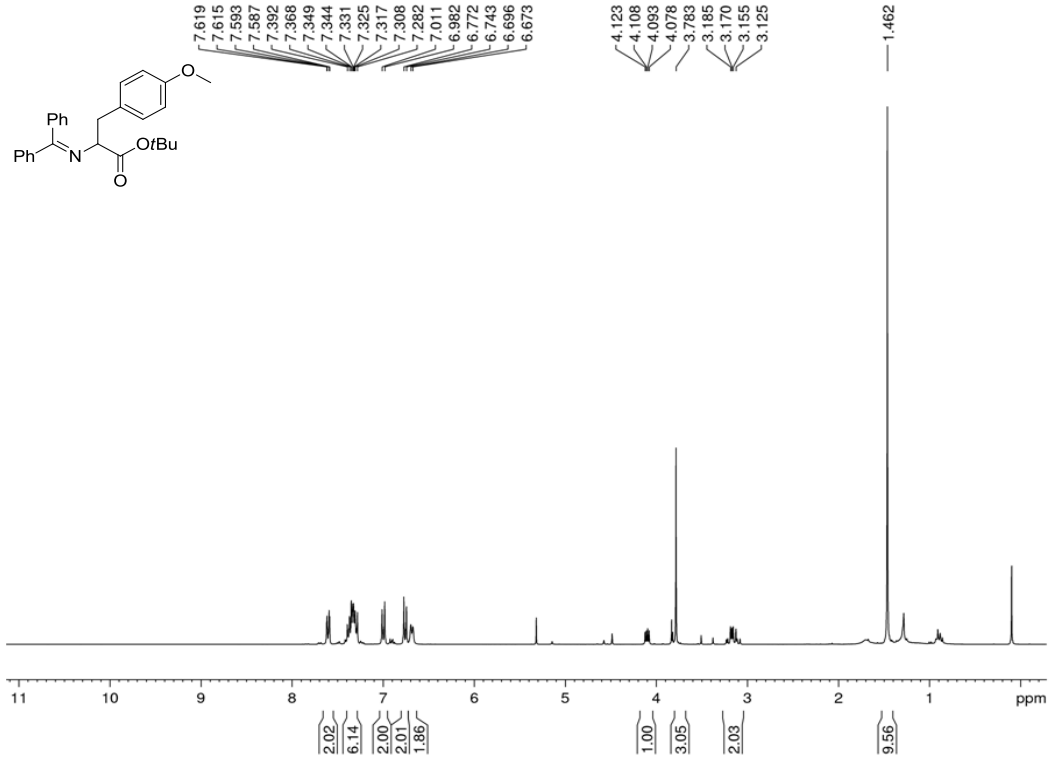
^{1}H NMR spectrum of **101h** in $CDCl_3$



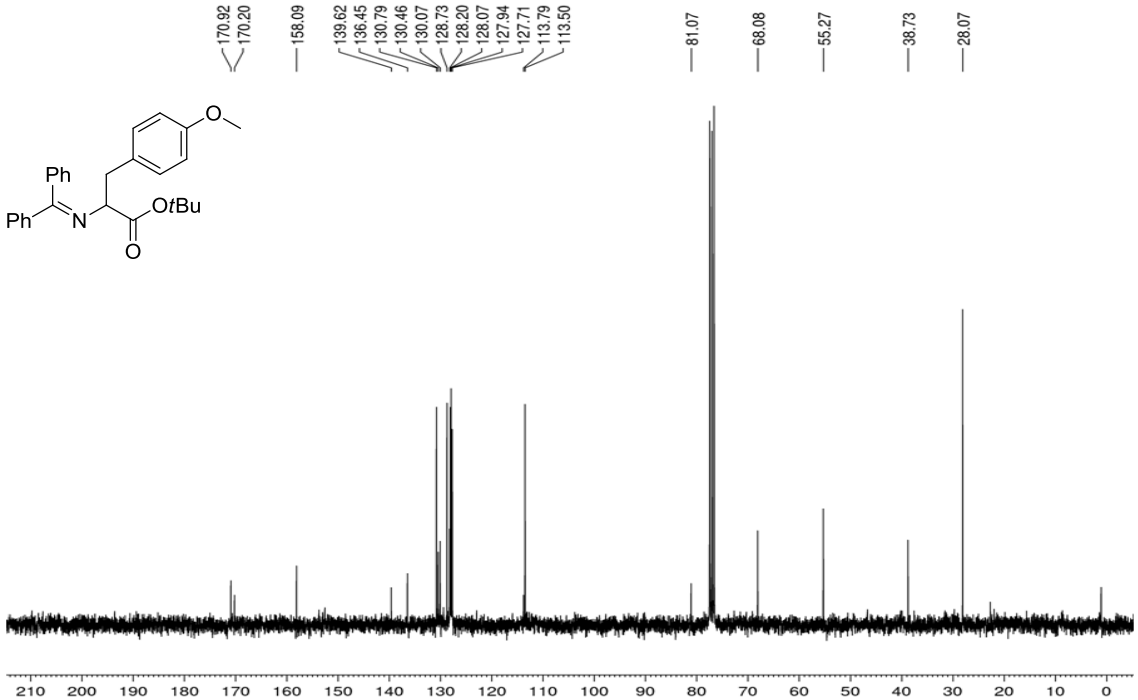
^{13}C NMR spectrum of **101h** in $CDCl_3$



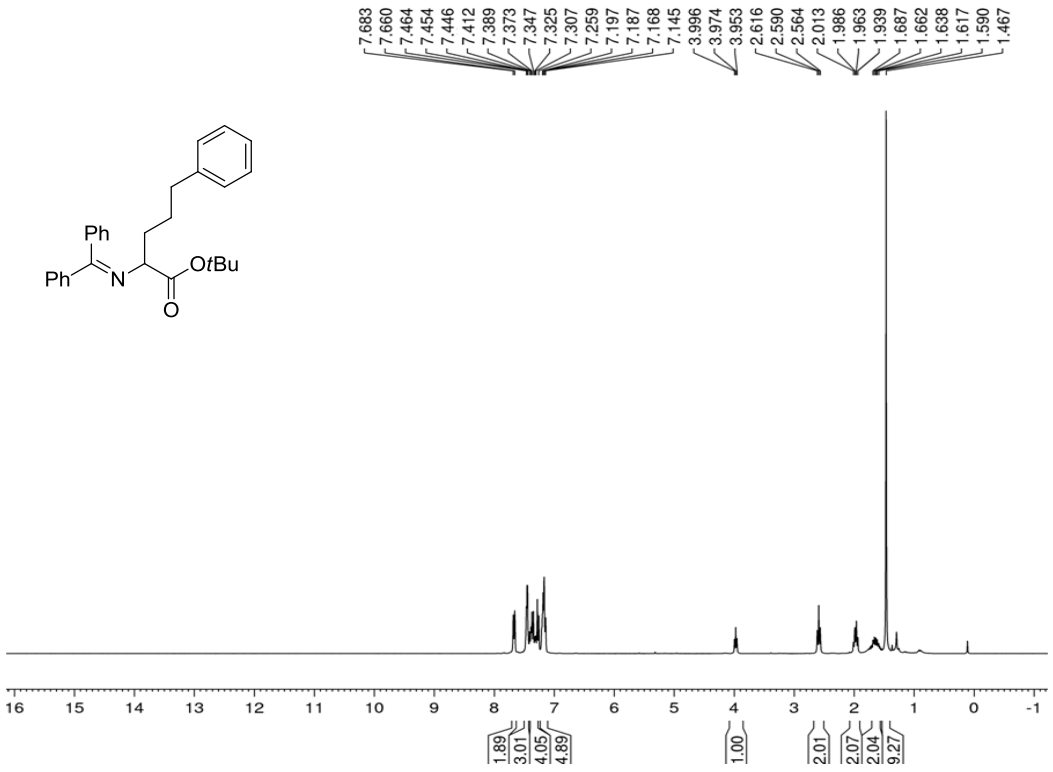
^{1}H NMR spectrum of **101e** in $CDCl_3$



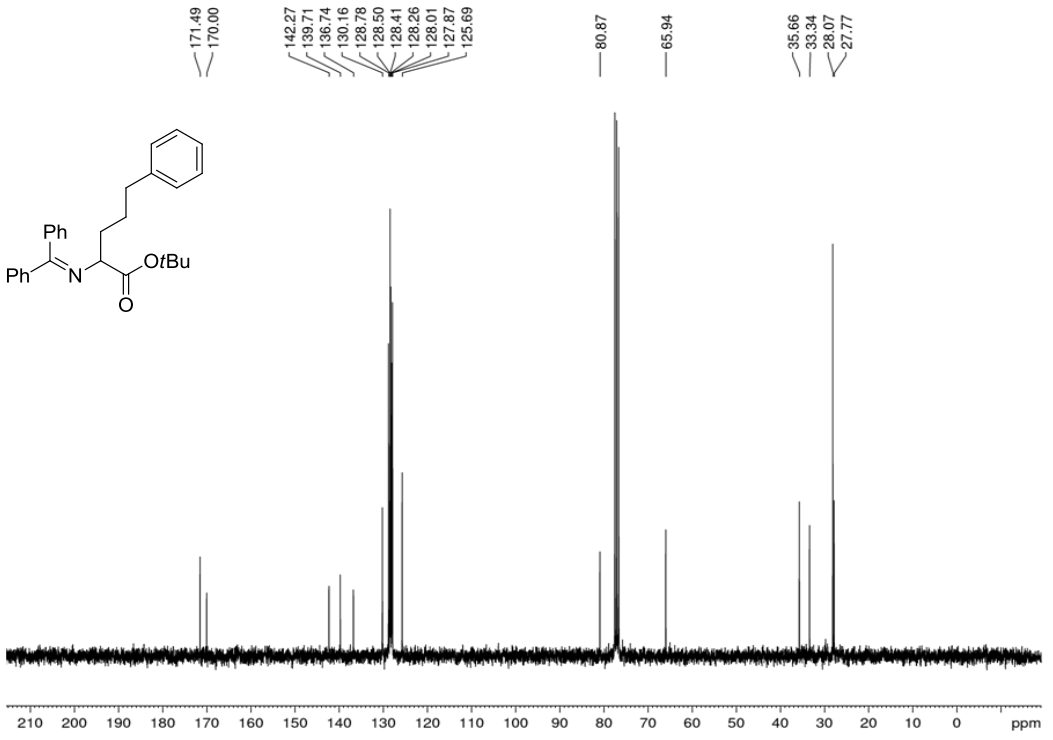
^{13}C NMR spectrum of **101e** in $CDCl_3$



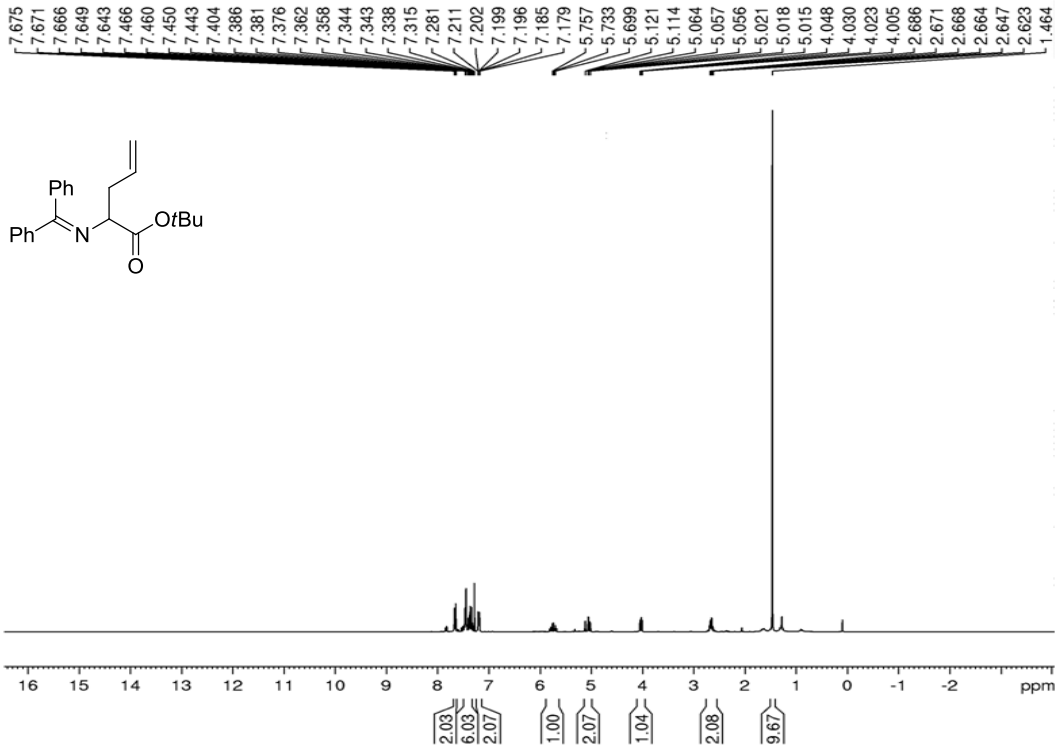
^{1}H NMR spectrum of **101i** in $CDCl_3$



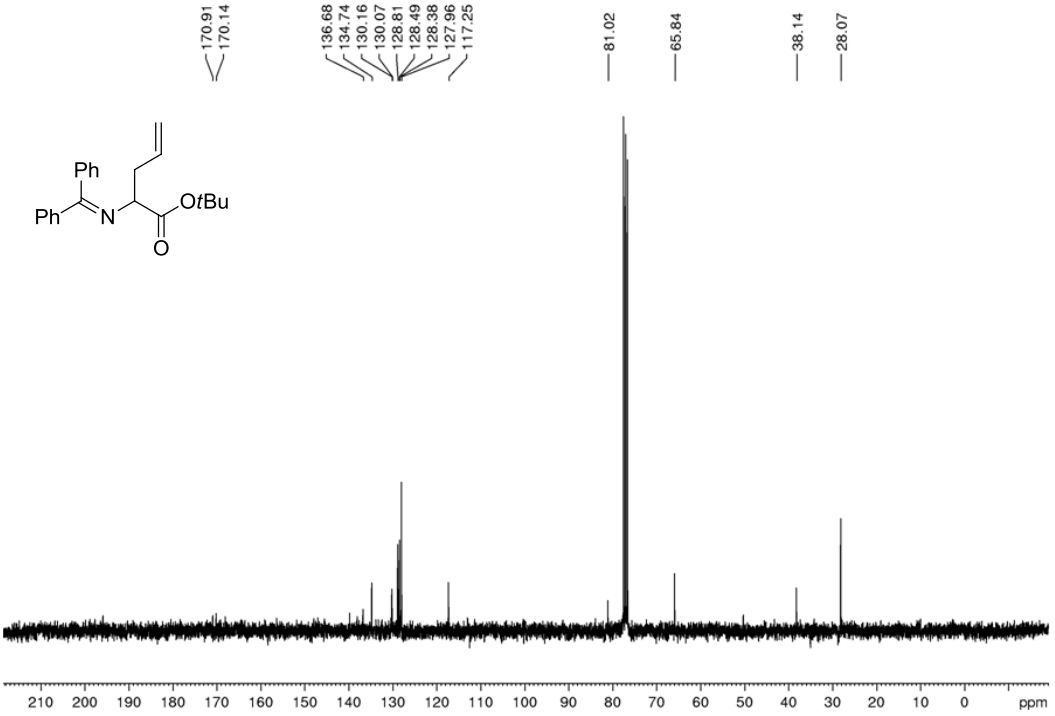
^{13}C NMR spectrum of **101i** in $CDCl_3$



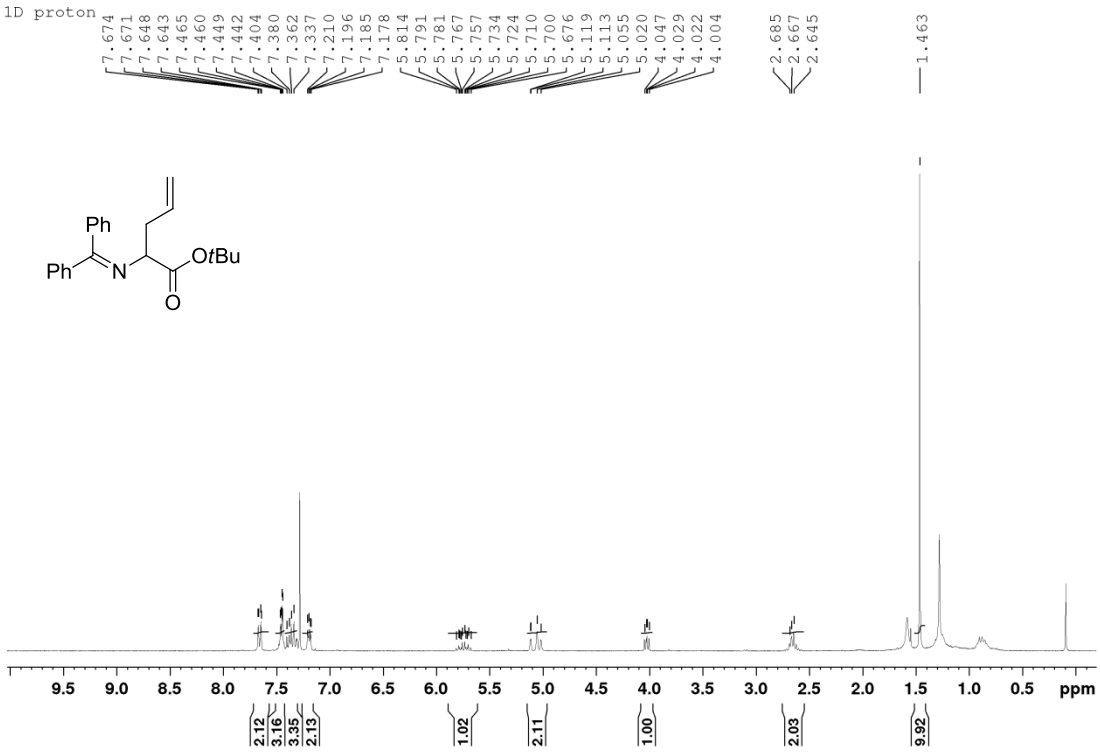
^{1}H NMR spectrum of **101j** in $CDCl_3$



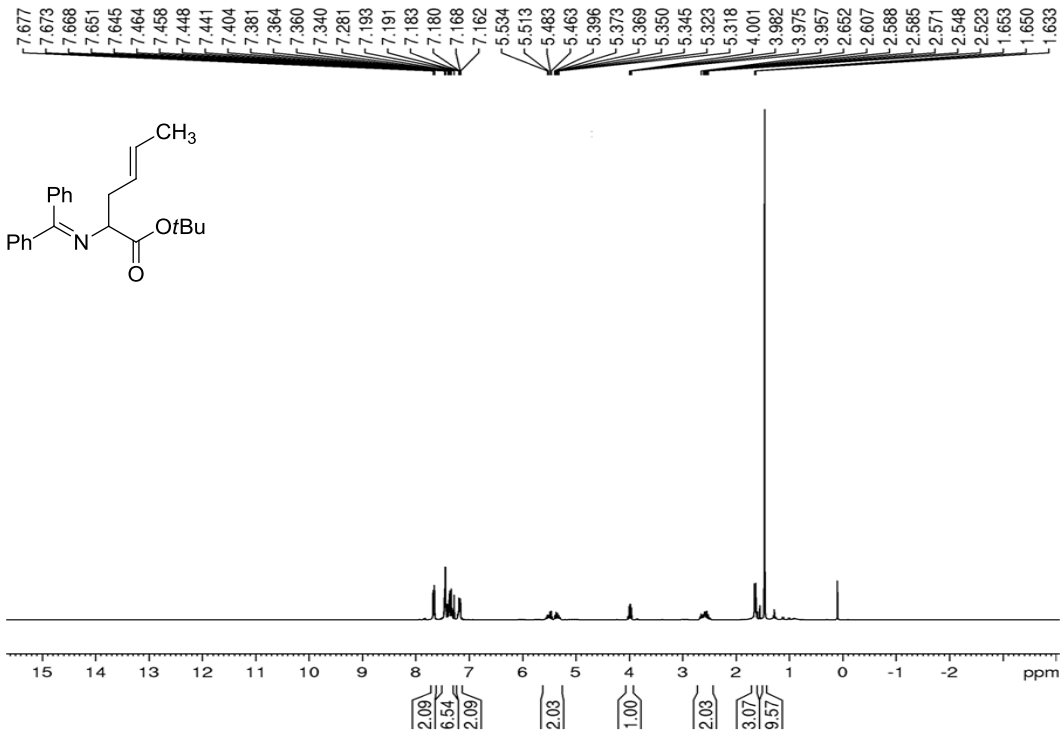
^{13}C NMR spectrum of **101j** in $CDCl_3$



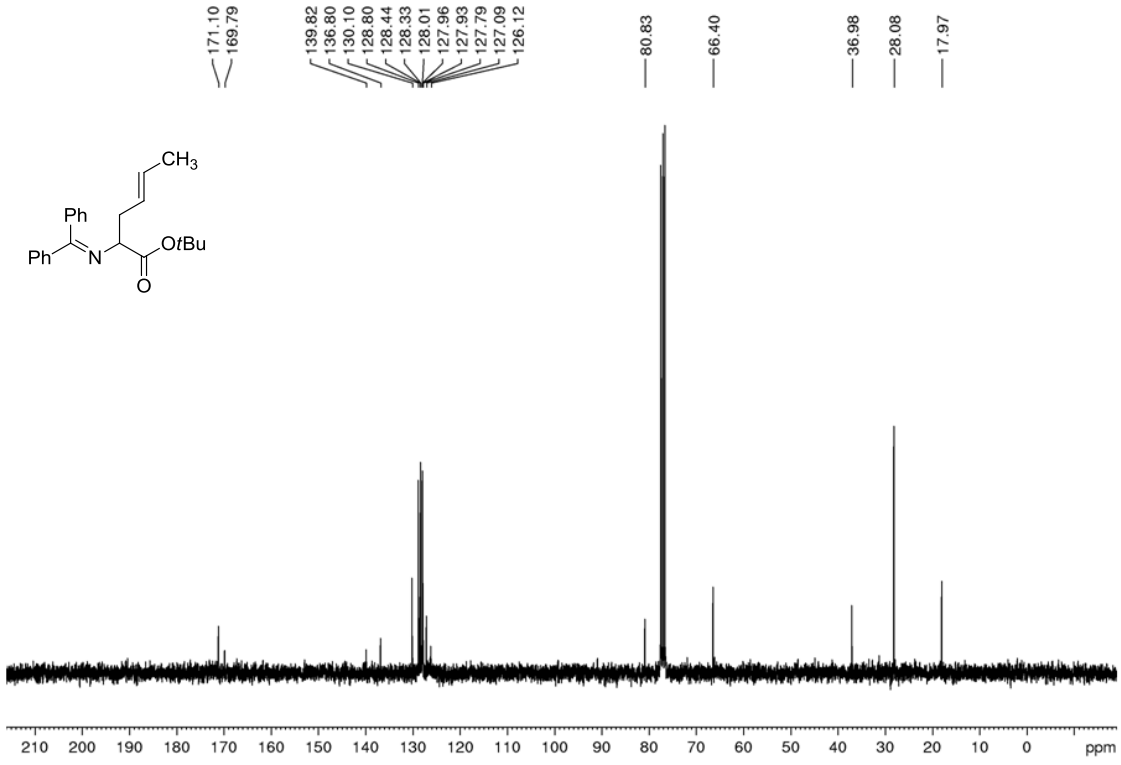
^{1}H NMR spectrum of **101k** in $CDCl_3$



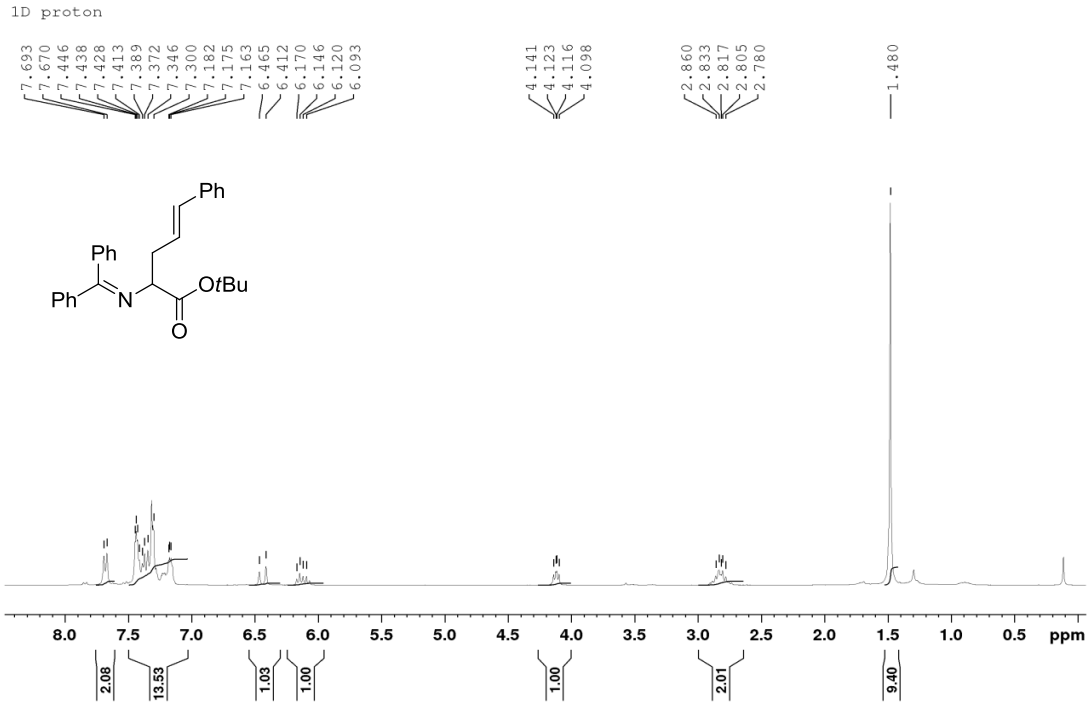
^{1}H NMR spectrum of **101l** in $CDCl_3$



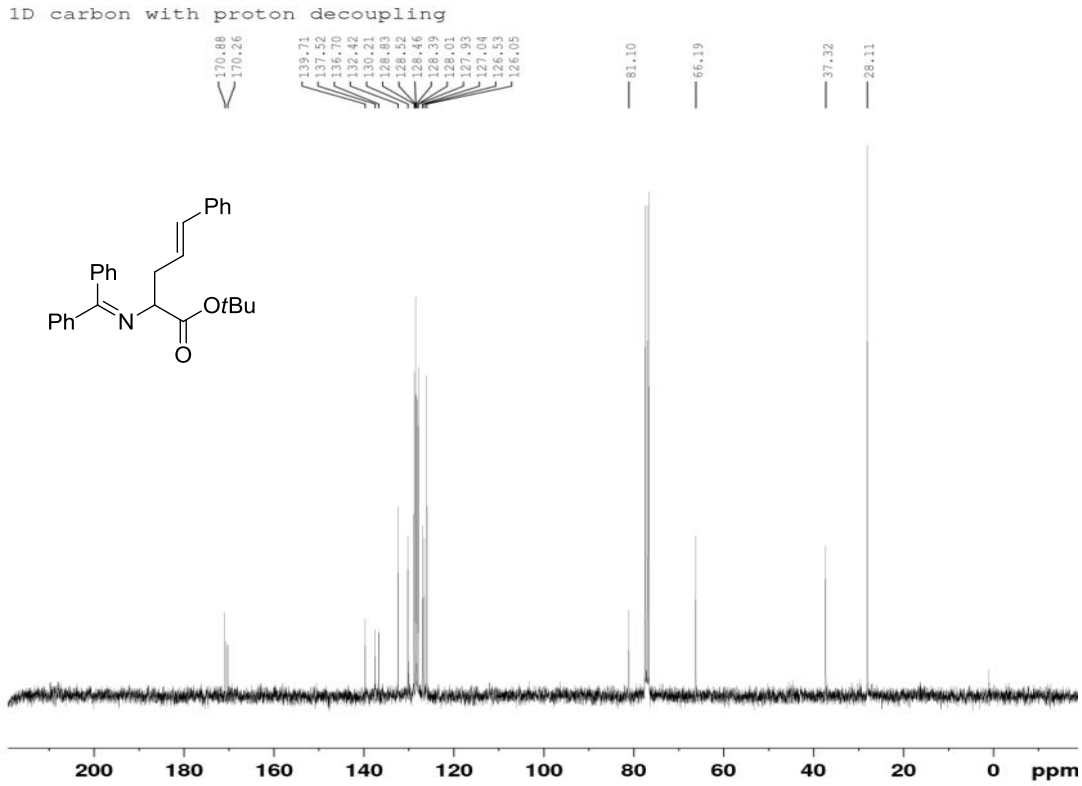
^{13}C NMR spectrum of **101l** in $CDCl_3$



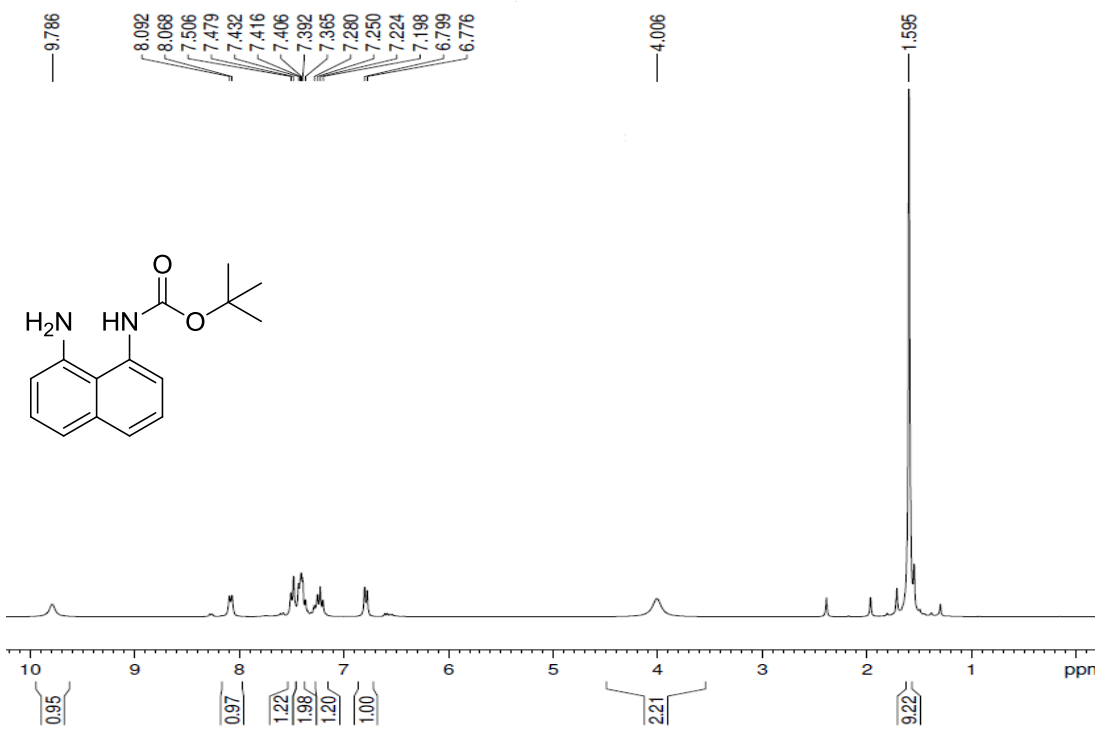
^{1}H NMR spectrum of **101m** in $CDCl_3$



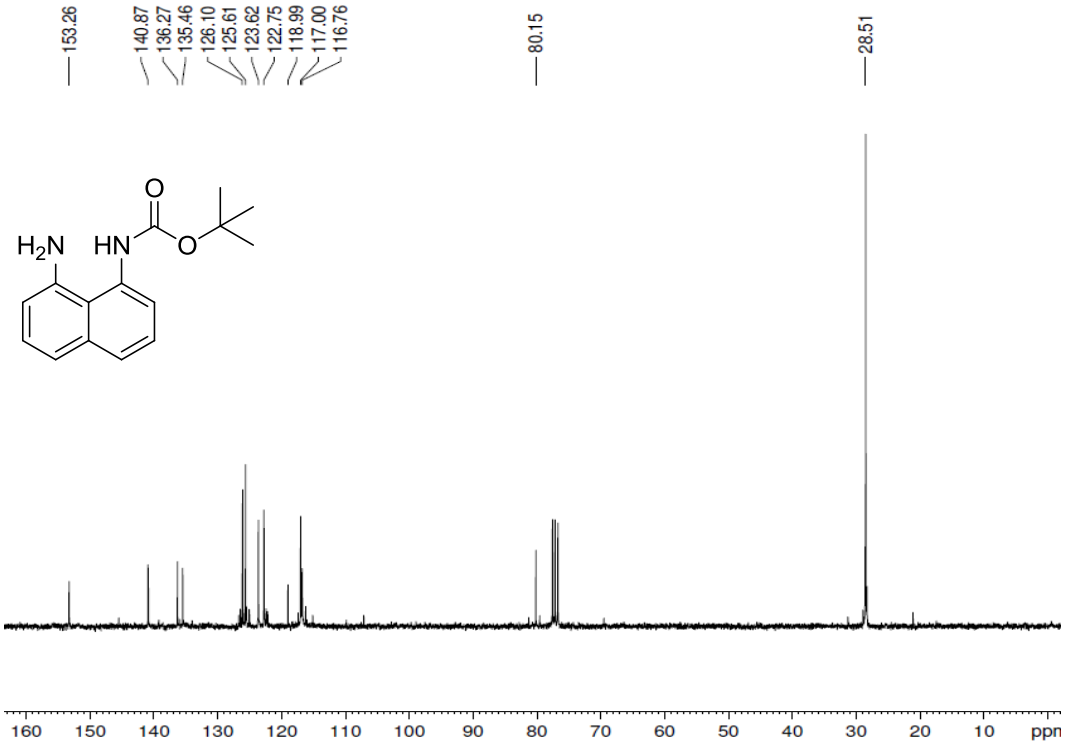
^{13}C NMR spectrum of **101m** in $CDCl_3$



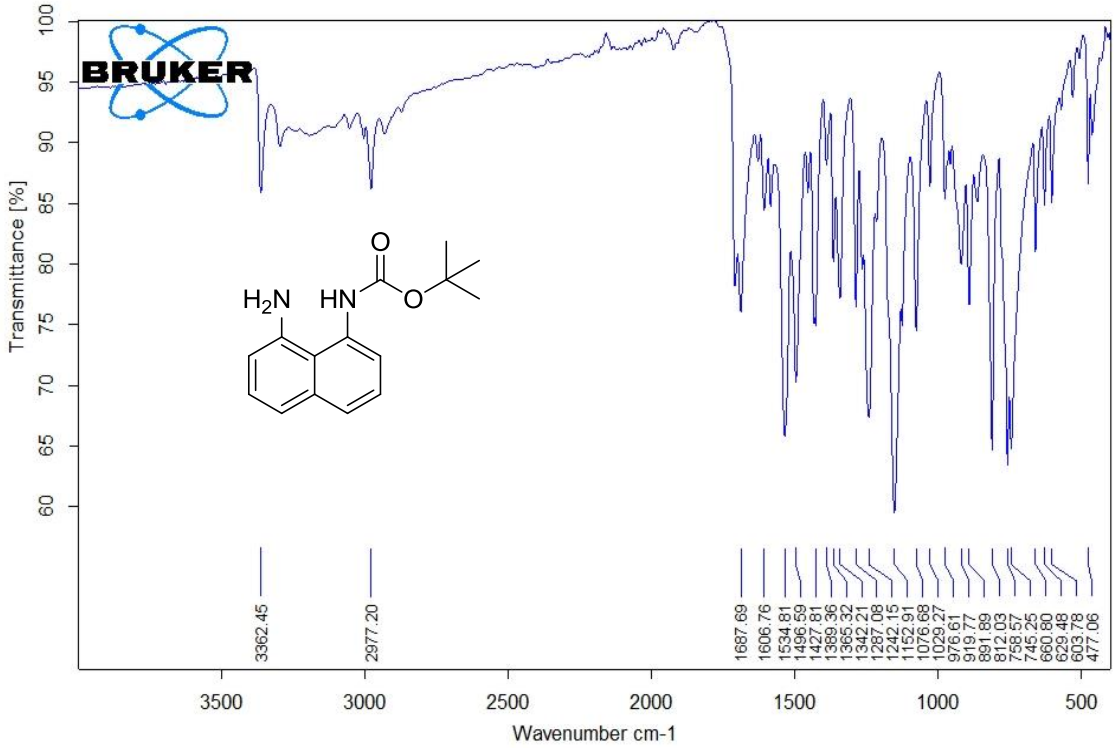
^{1}H NMR spectrum of **107m** in $CDCl_3$



^{13}C NMR spectrum of **107m** in $CDCl_3$



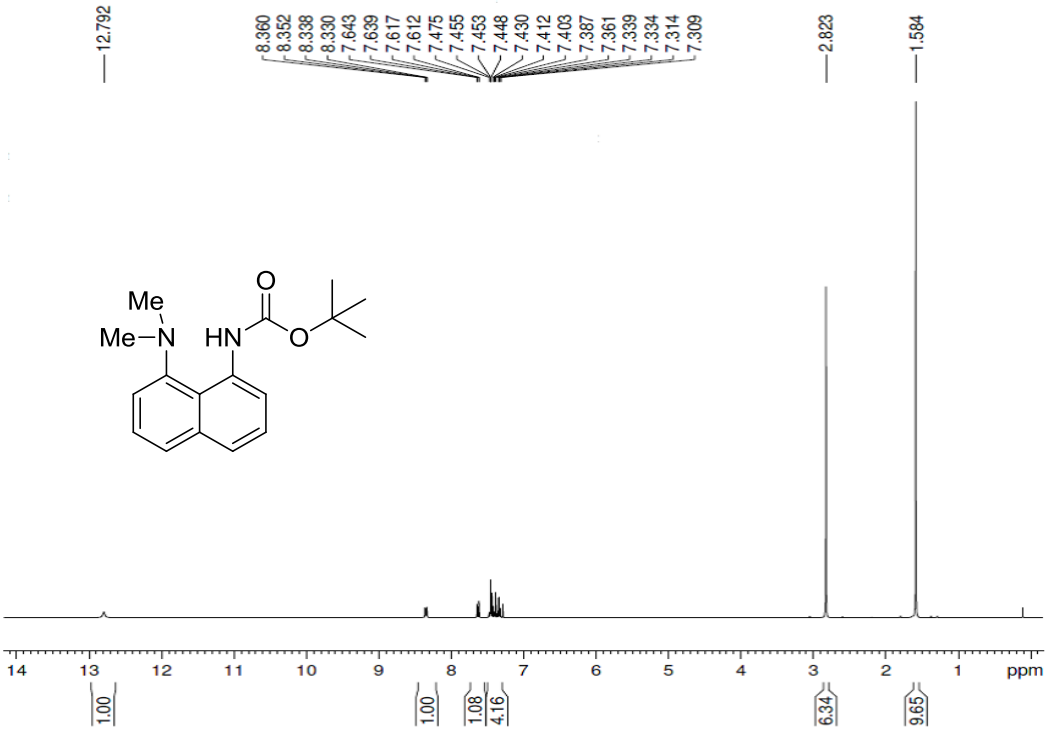
IR Spectrum of 107



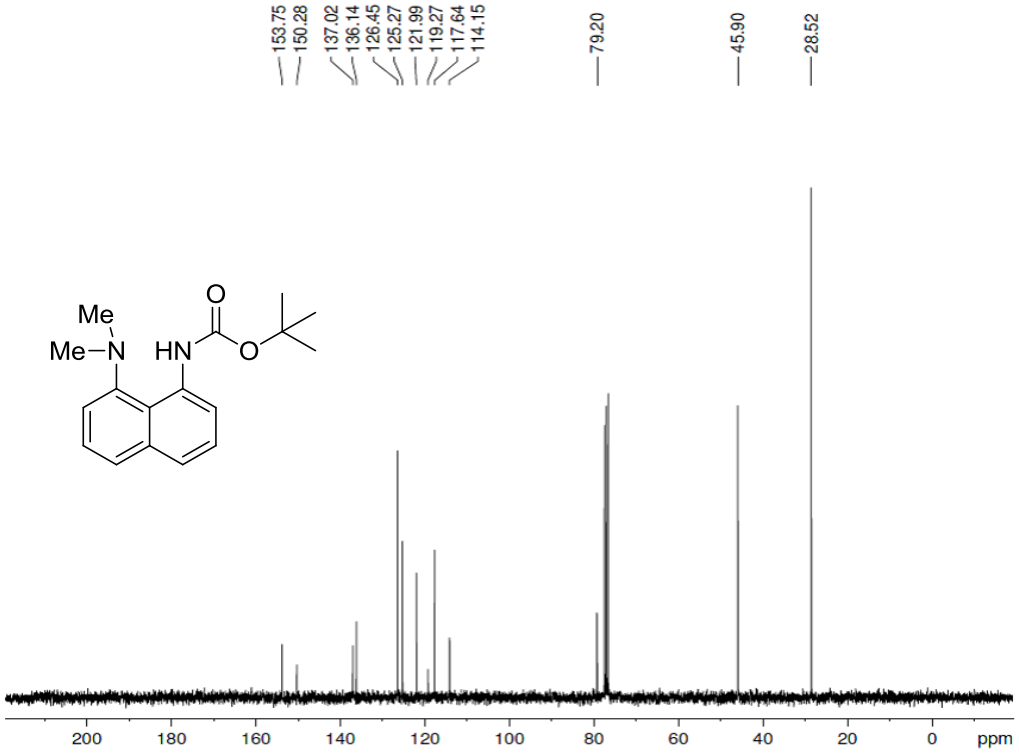
C:\Users\Administrator\Desktop\Student Spectra\MonoBoc.0	Sample description	Instrument type and / or accessory	25/06/2015

Paqe 1/1

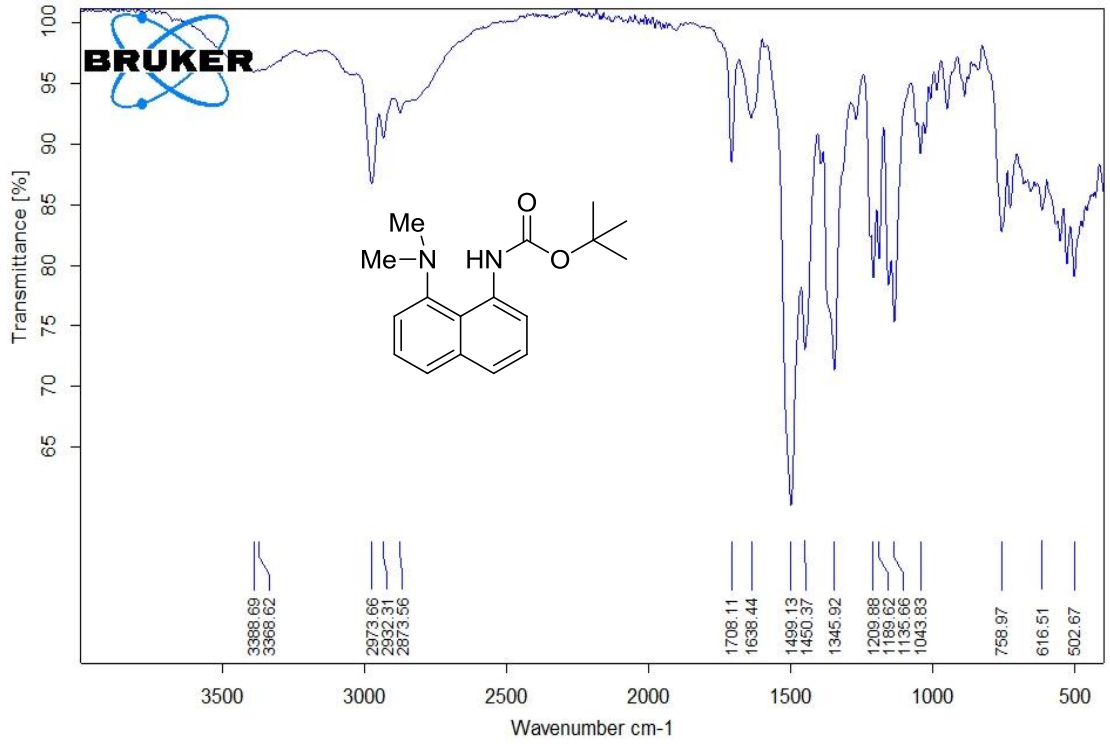
^{1}H NMR spectrum of **108** in $CDCl_3$



^{13}C NMR spectrum of **108** in $CDCl_3$



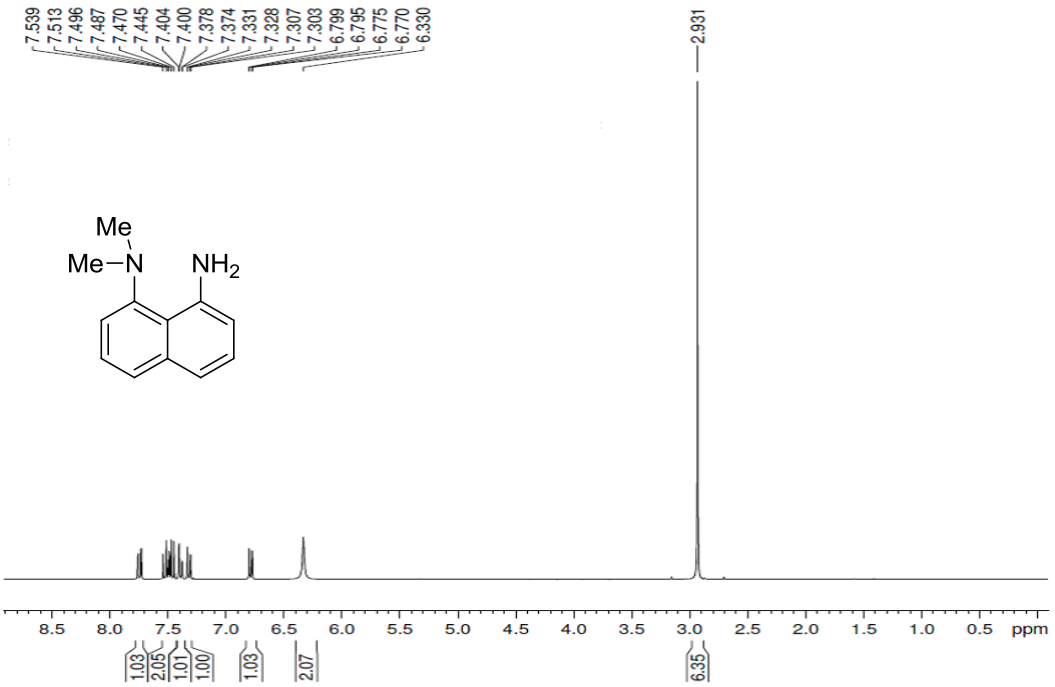
IR Spectrum of 108



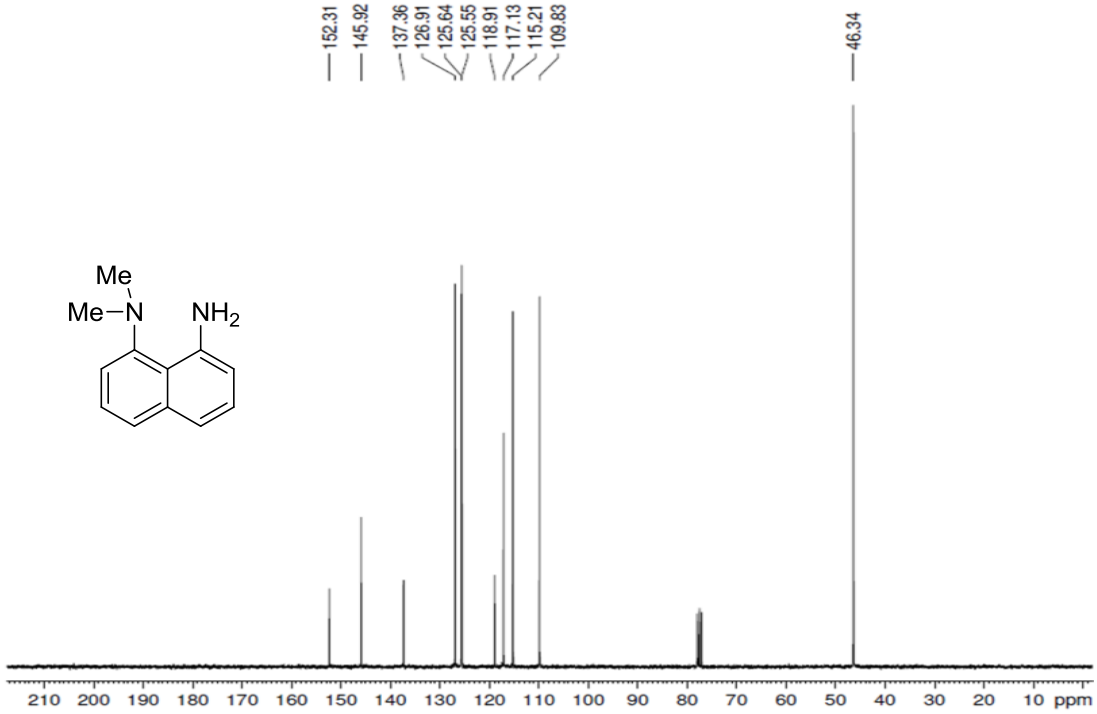
C:\Users\Administrator\Desktop\Student Spectra\Sample description.1296	Sample description	Instrument type and / or accessory	06/06/2014

Page 1/1

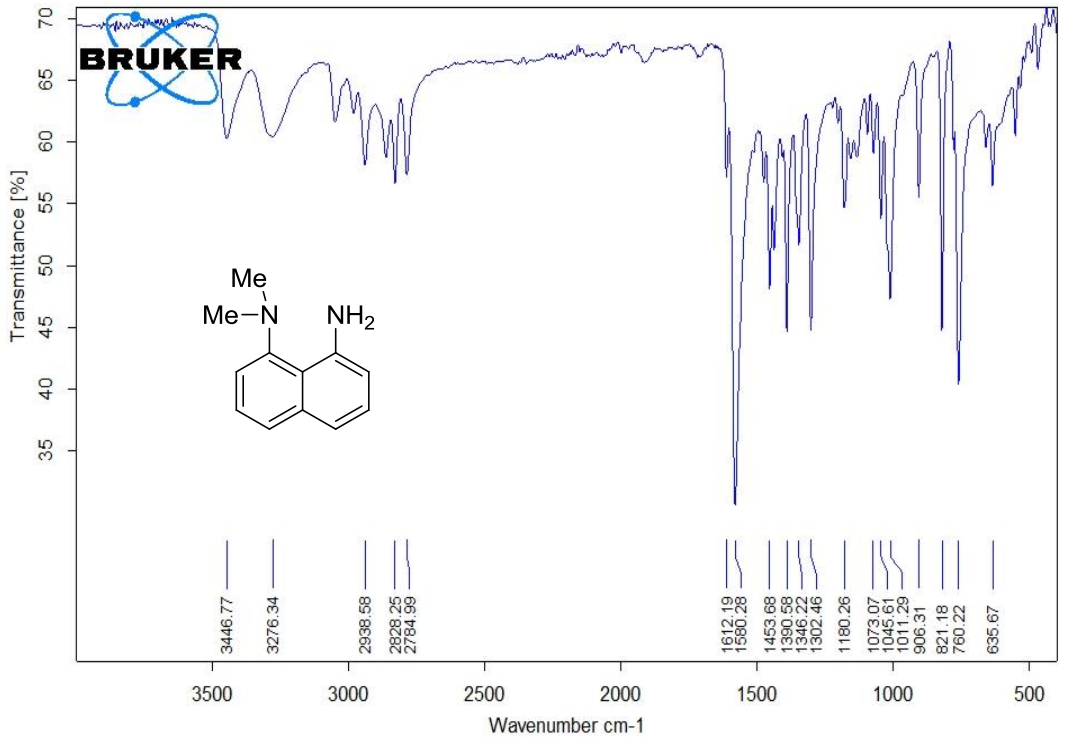
^{1}H NMR spectrum of **109** in $CDCl_3$



^{13}C NMR spectrum of **109** in $CDCl_3$



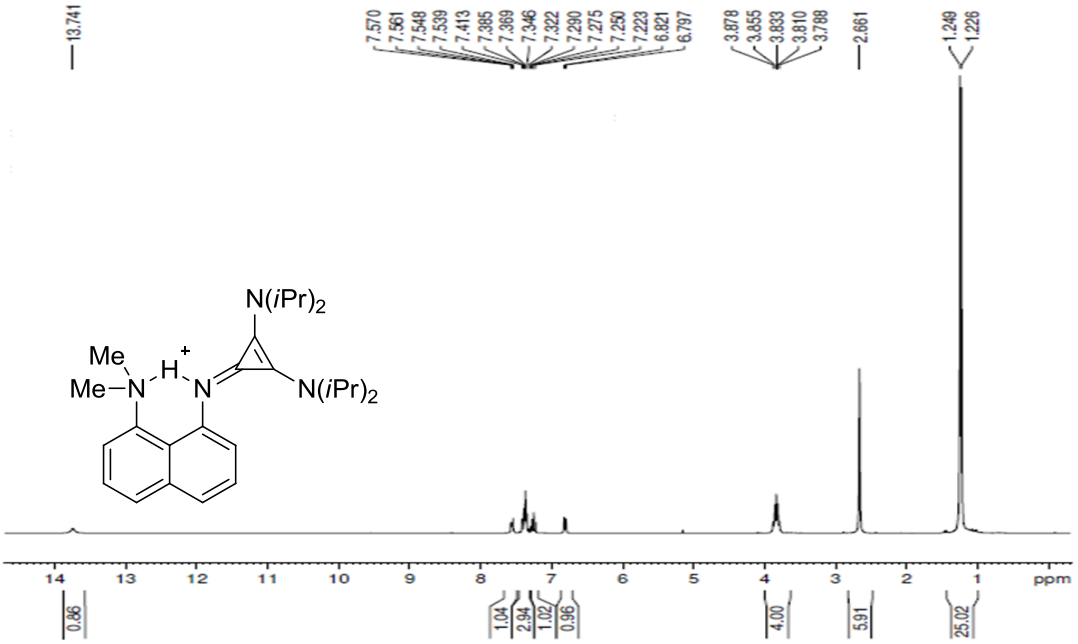
IR Spectrum of 109



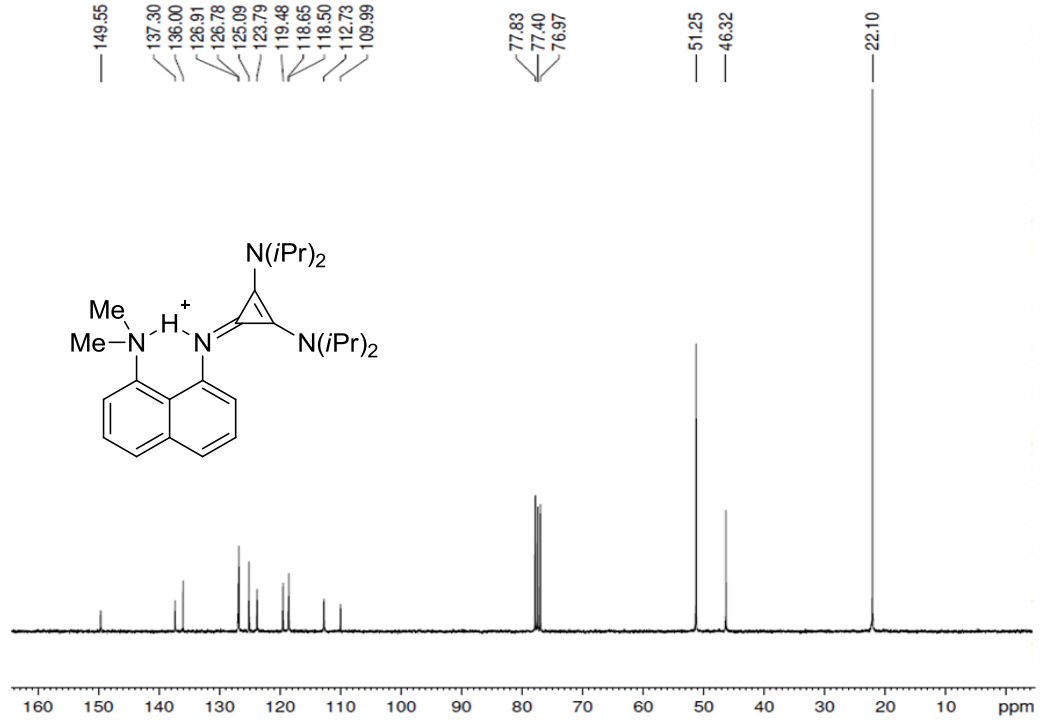
C:\Users\Administrator\Desktop\Student Spectra\LB-Dimethyl.0	LB-Dimethyl	Instrument type and / or accessory	16/06/2014

Paqe 1/1

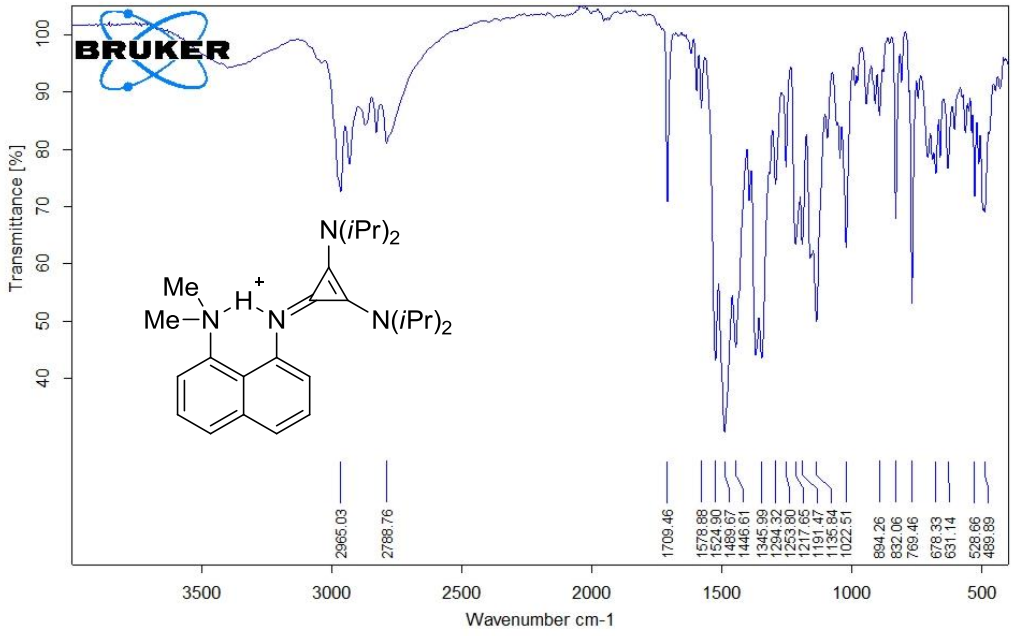
^{1}H NMR spectrum of **102** in $CDCl_3$



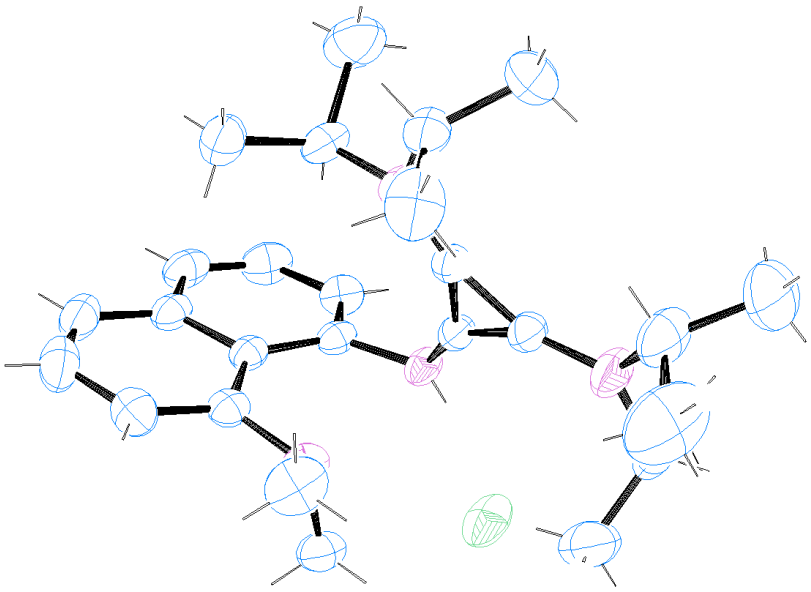
^{13}C NMR spectrum of **102** in $CDCl_3$



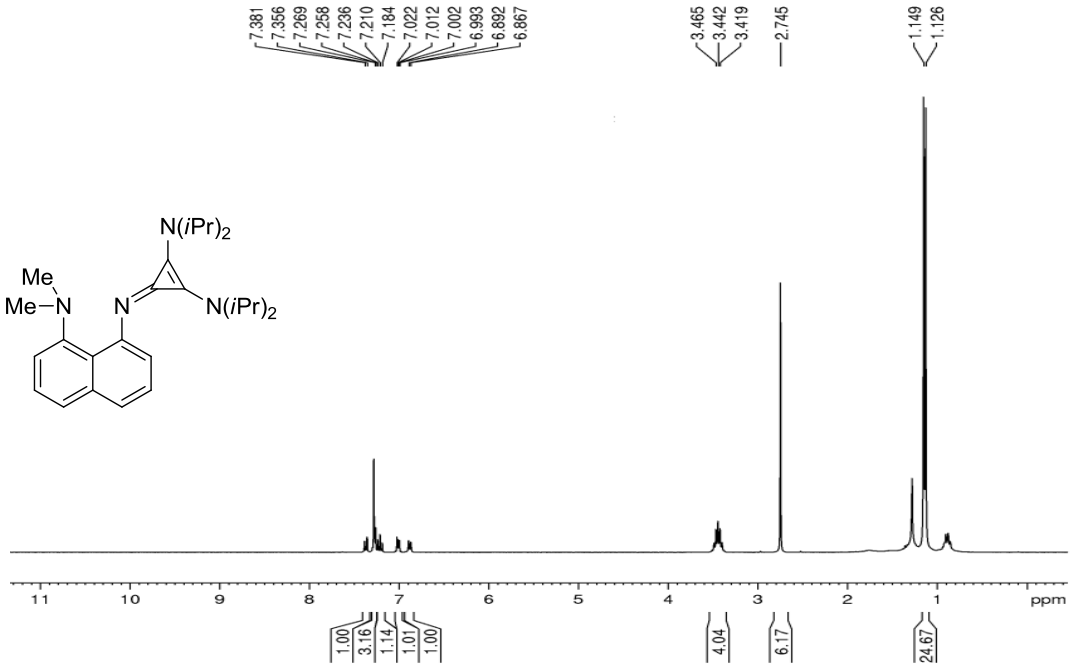
IR Spectrum of 102



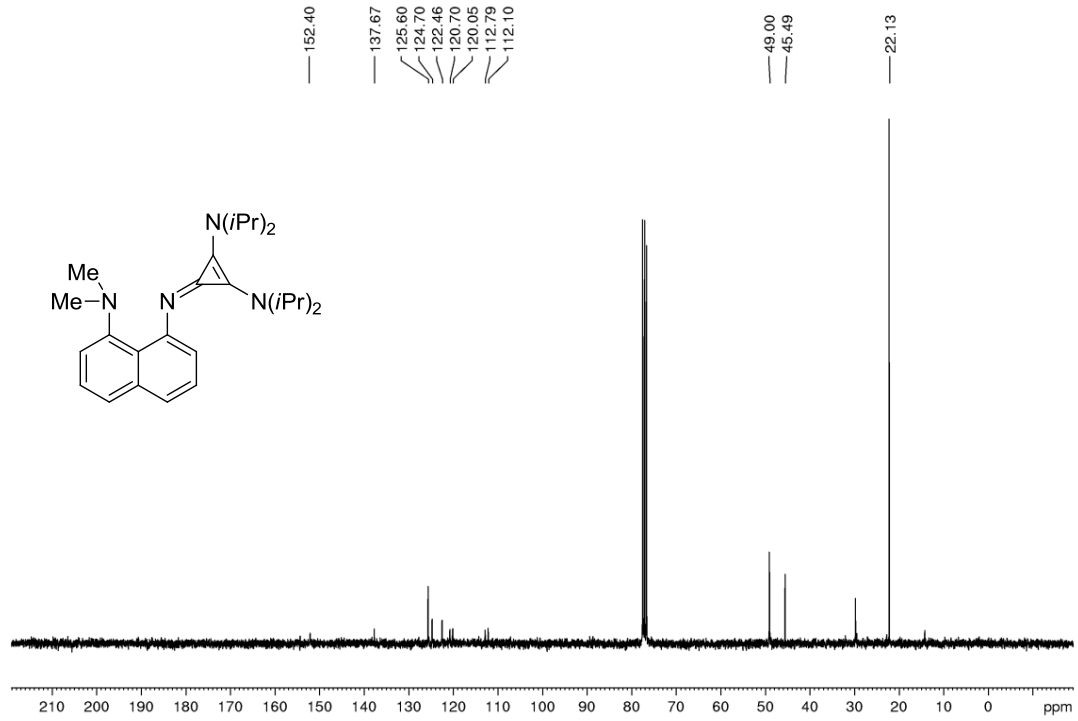
Thermal ellipsoid (percent probability: 50%) plot of the X-ray diffraction structure of compound 102 generated using Ortep3



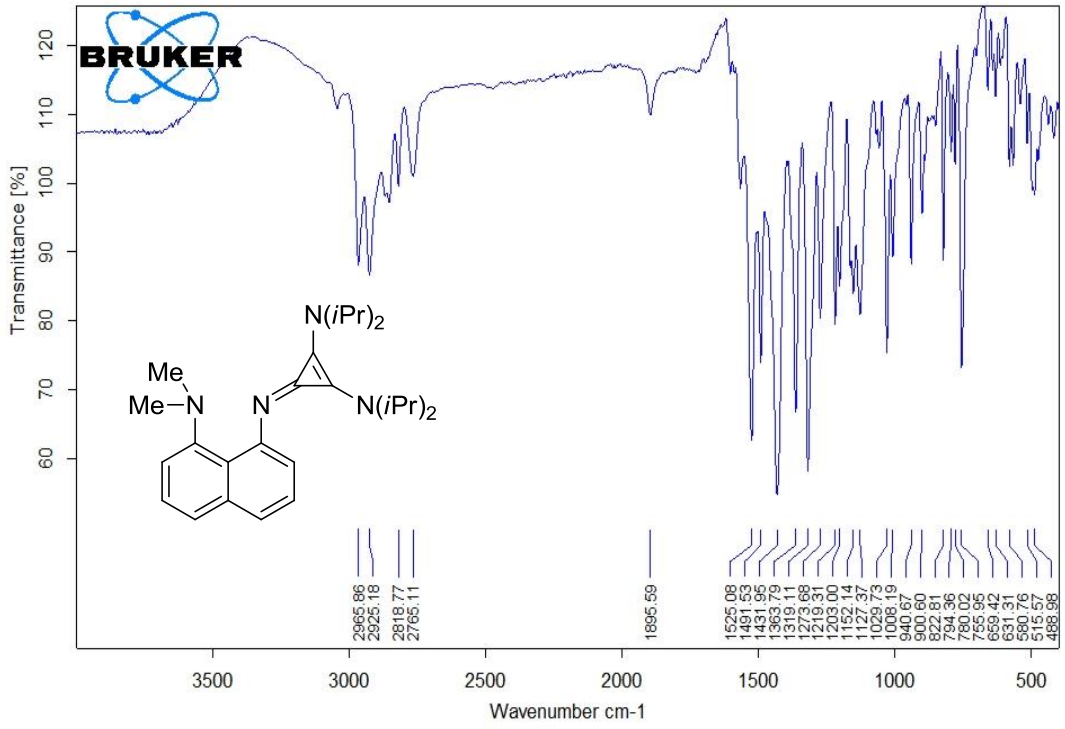
^{1}H NMR spectrum of **95** in $CDCl_3$



^{13}C NMR spectrum of **95** in $CDCl_3$



IR Spectrum of 95

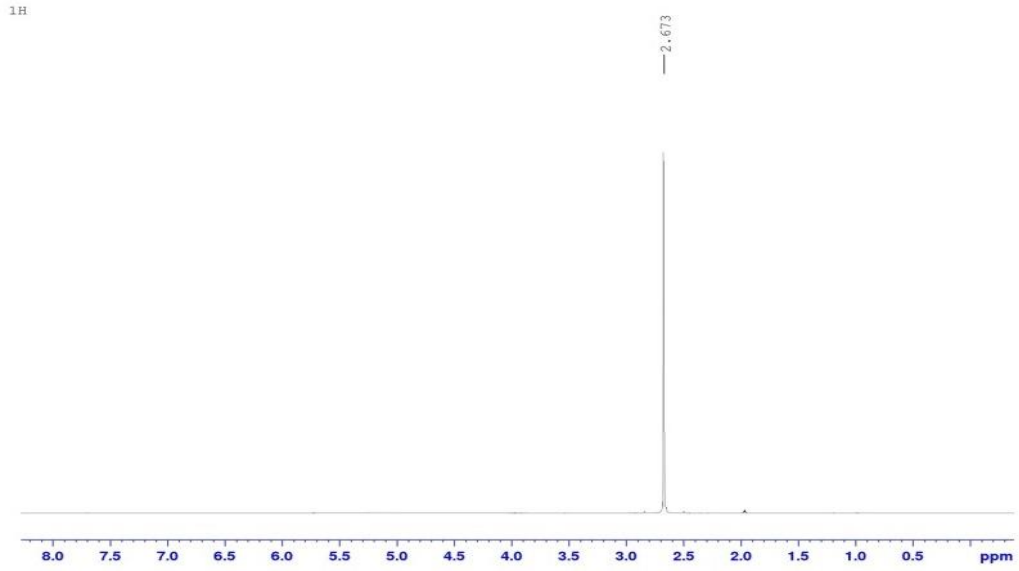


C:\Users\Administrator\Desktop\Student Spectra\Janus freebase.0	Sample description	Instrument type and / or accessory	25/06/2015

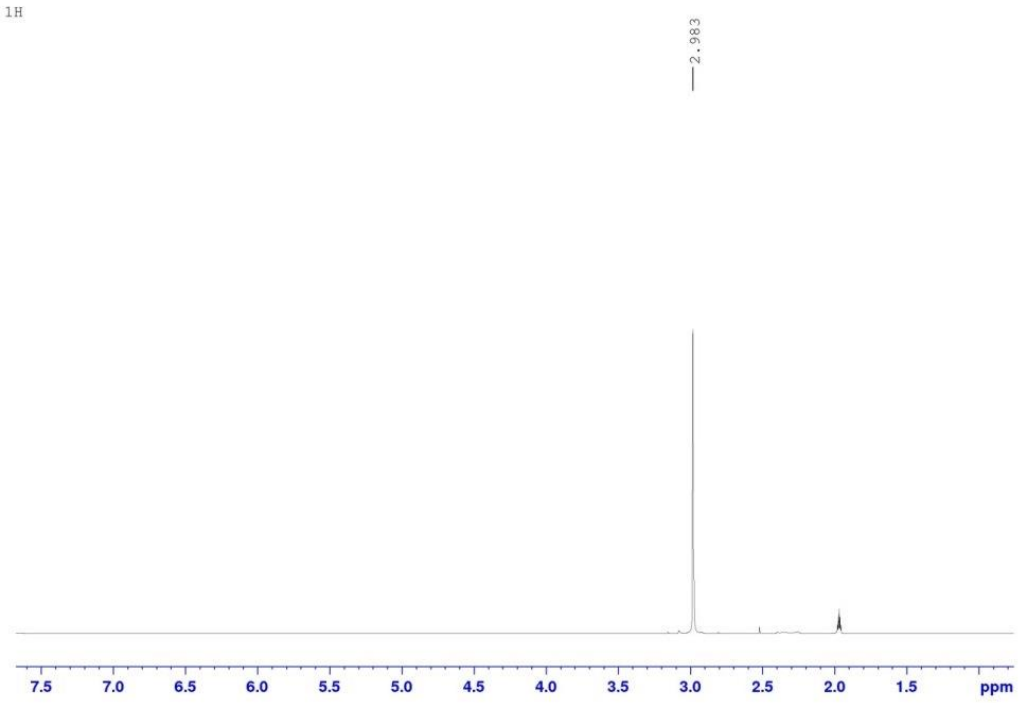
Paqe 1/1

^{1}H NMR for pK_a measurements:

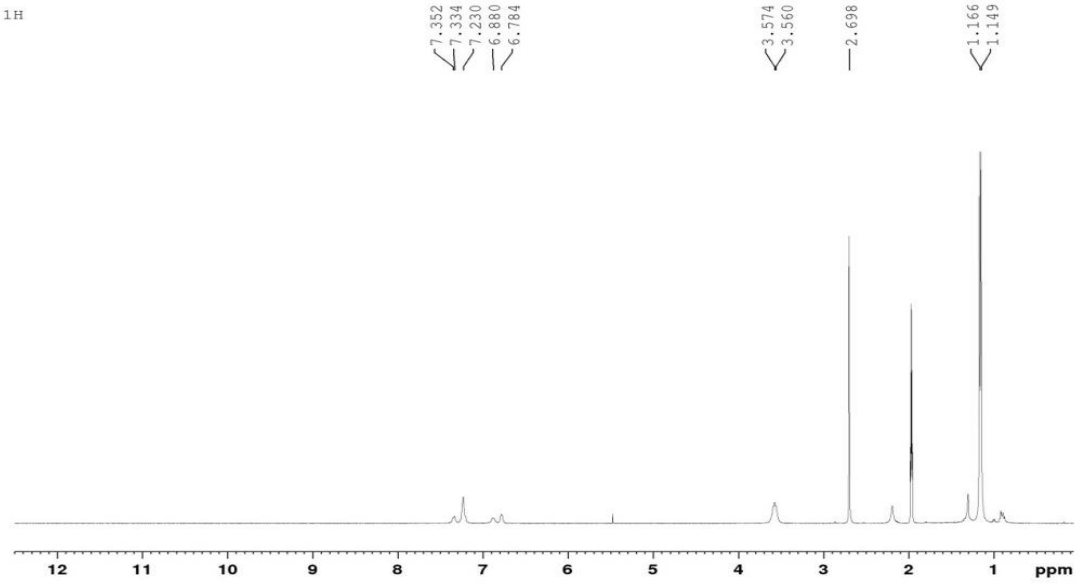
^{1}H NMR of TMG in MeCN-d_3



^{1}H NMR of TMG•HCl in MeCN-d_3

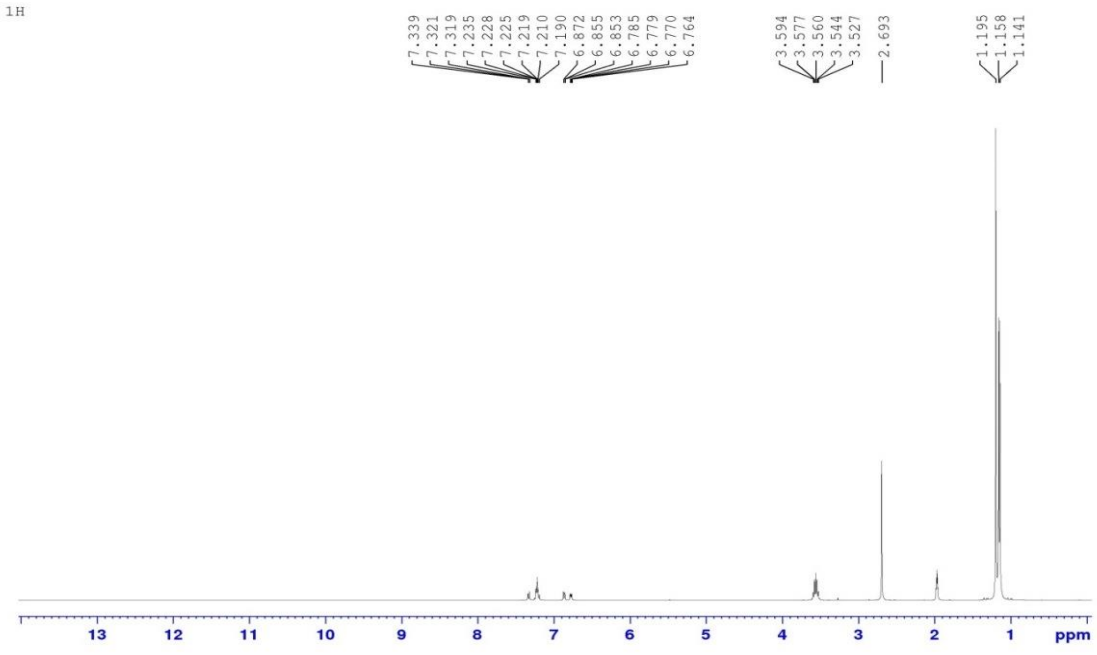


^{1}H NMR of **95** in MeCN-d_3

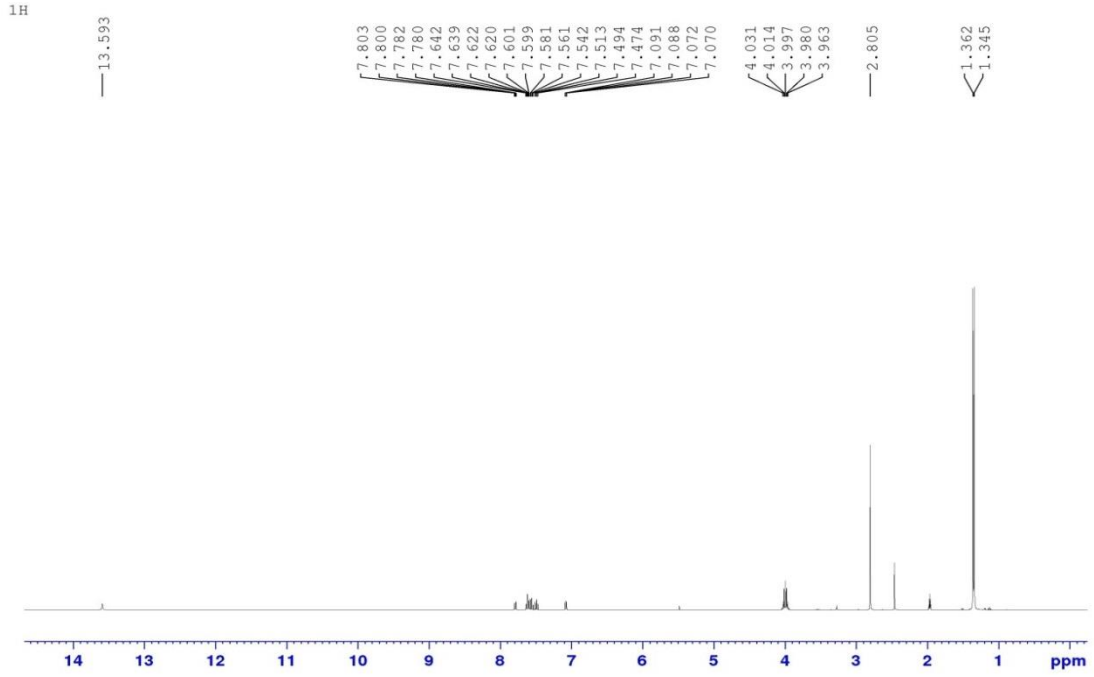


^{1}H NMR of **95** in MeCN-d_3

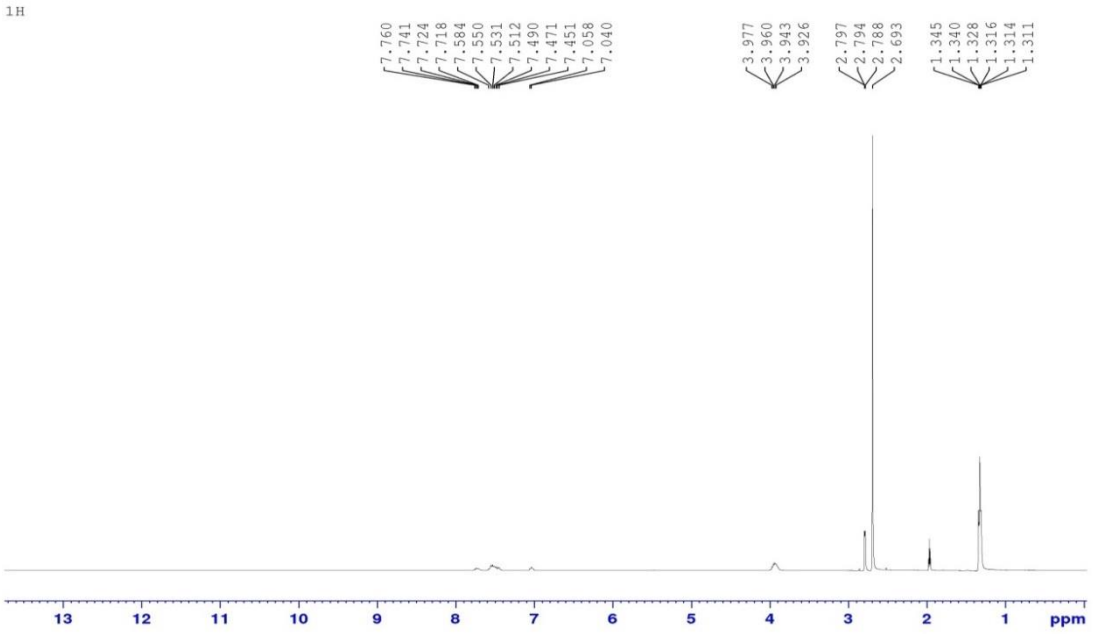
(generated by the addition of excess potassium *tert*-butoxide to a solution of **95** in MeCN-d_3)



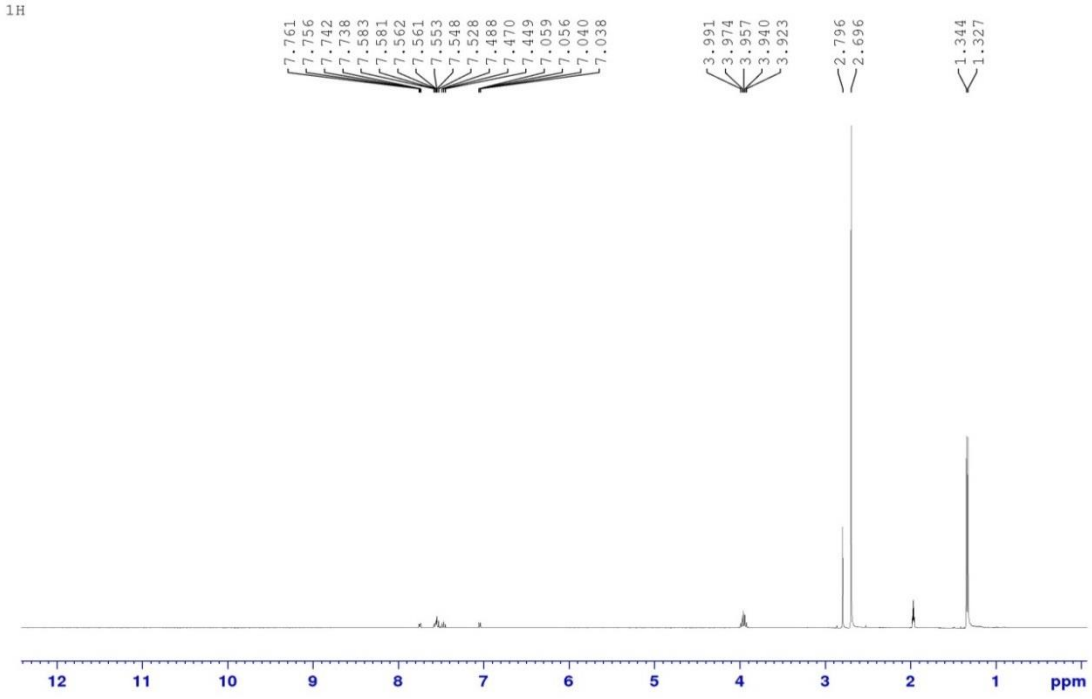
^{1}H NMR of **102** in MeCN-d_3



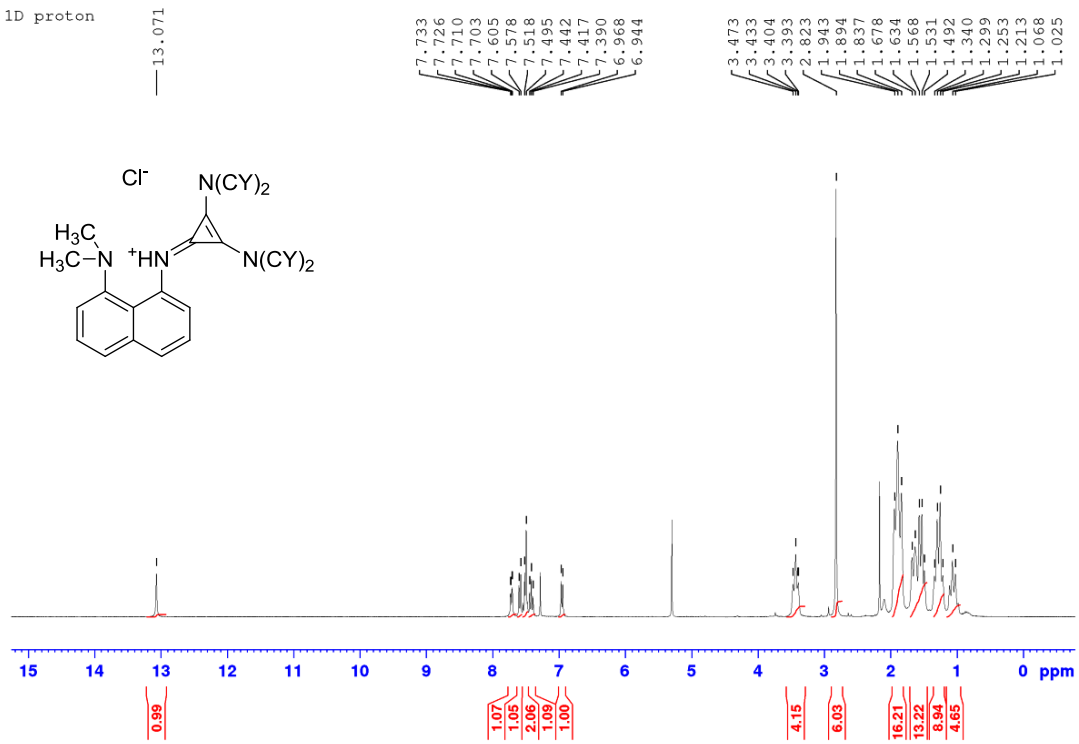
^{1}H NMR of TMG and **102** in MeCN-d_3



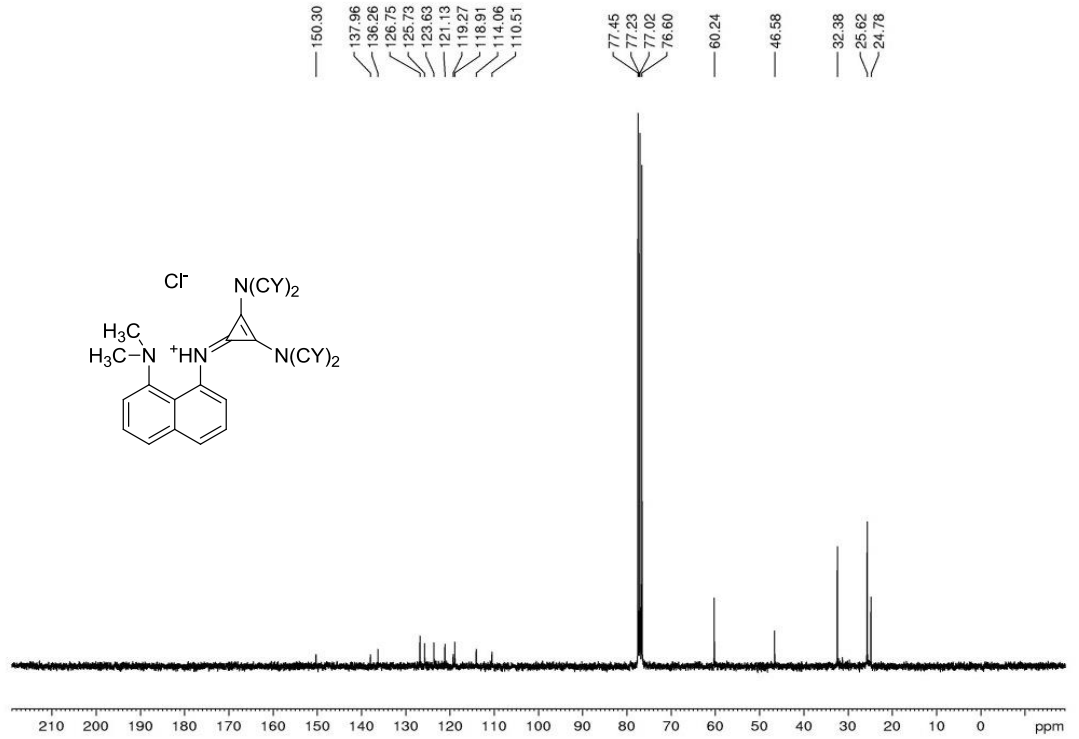
^{1}H NMR of TMG•HCl and **95** in MeCN-d_3



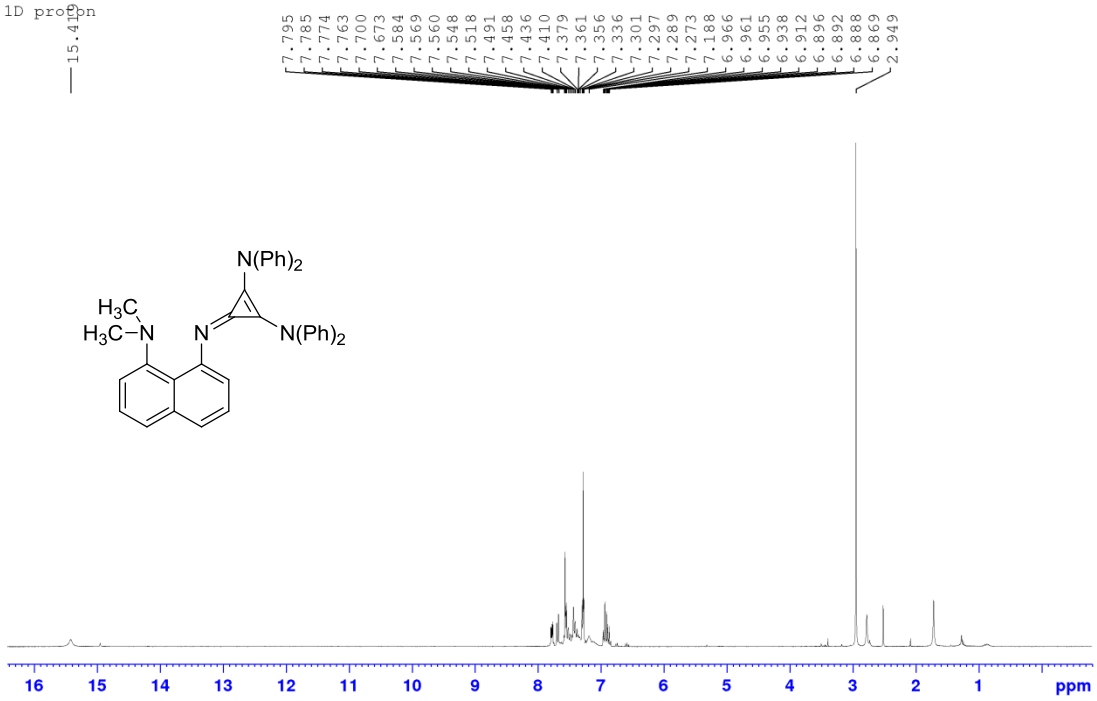
^{1}H NMR spectrum of **111** in $CDCl_3$



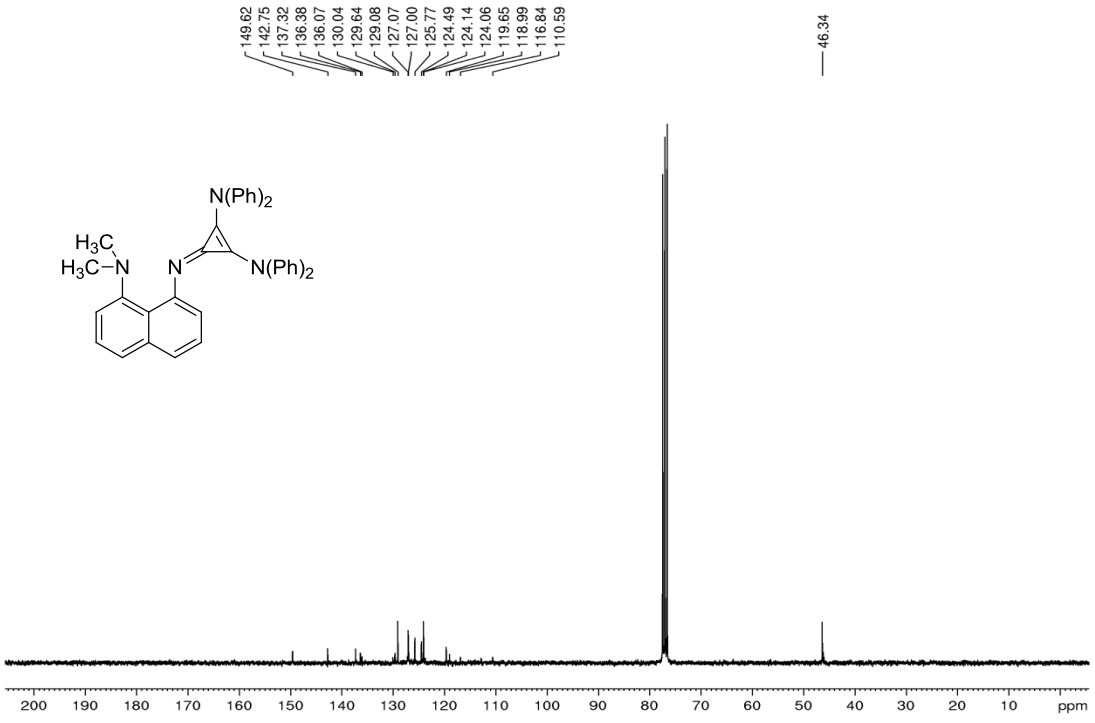
^{13}C NMR spectrum of **111** in $CDCl_3$



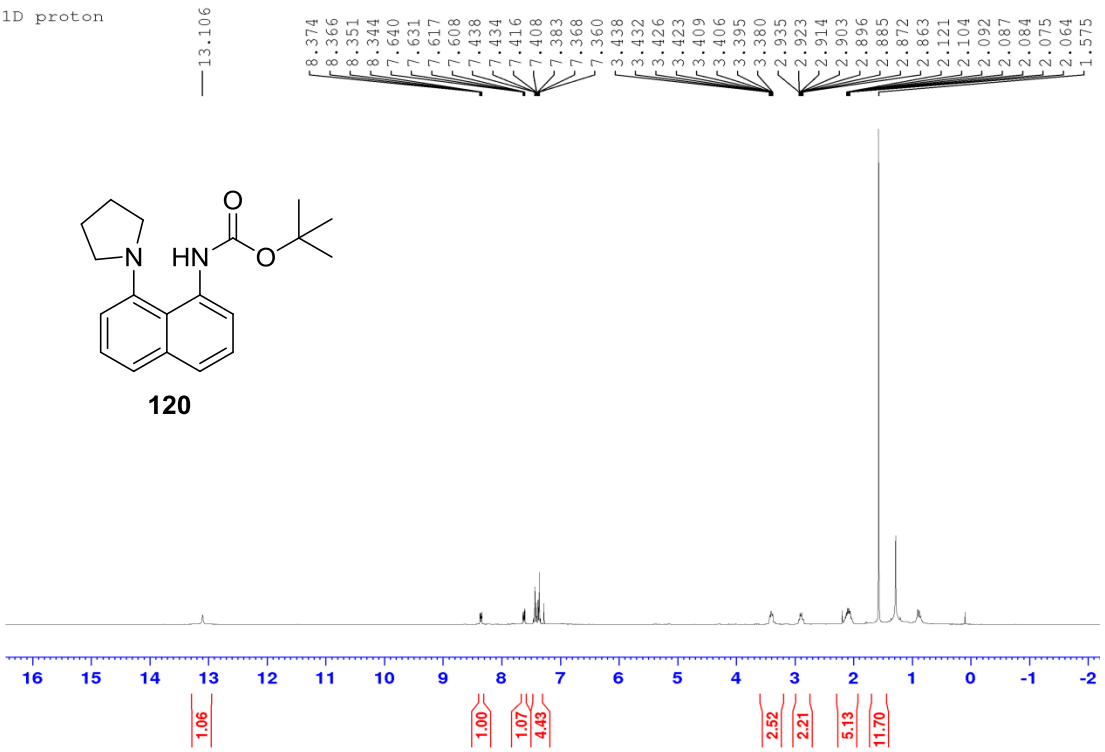
^{1}H NMR spectrum of **112** in $CDCl_3$



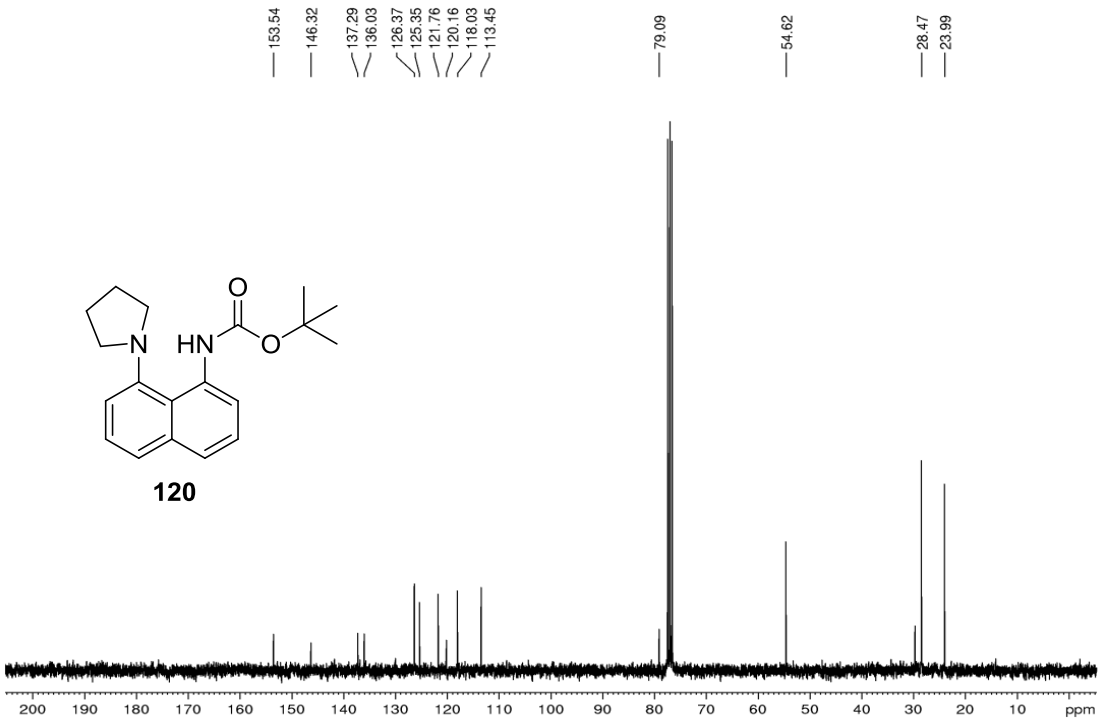
^{13}C NMR spectrum of **112** in $CDCl_3$



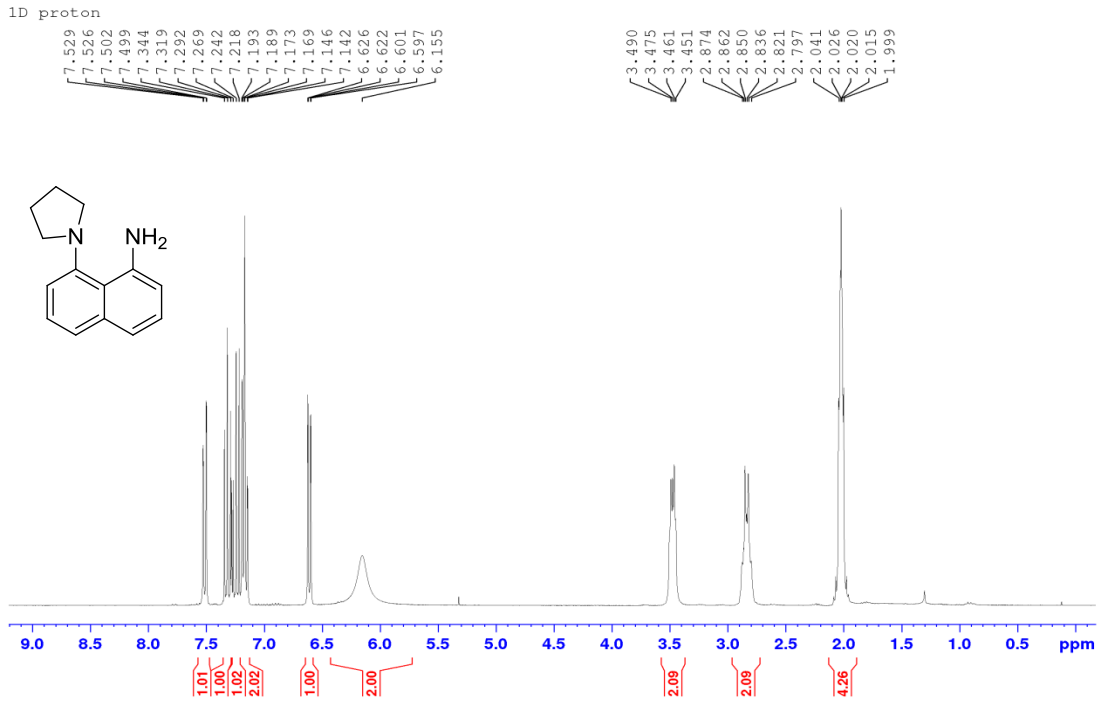
^{1}H NMR spectrum of **120** in $CDCl_3$



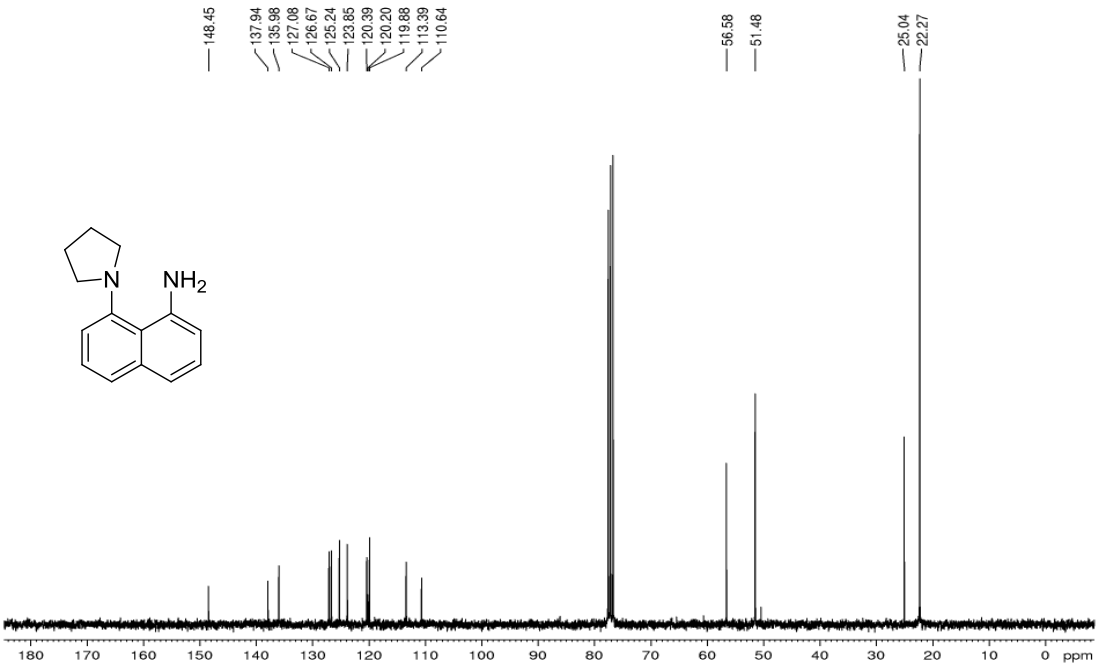
^{13}C NMR spectrum of **120** in $CDCl_3$



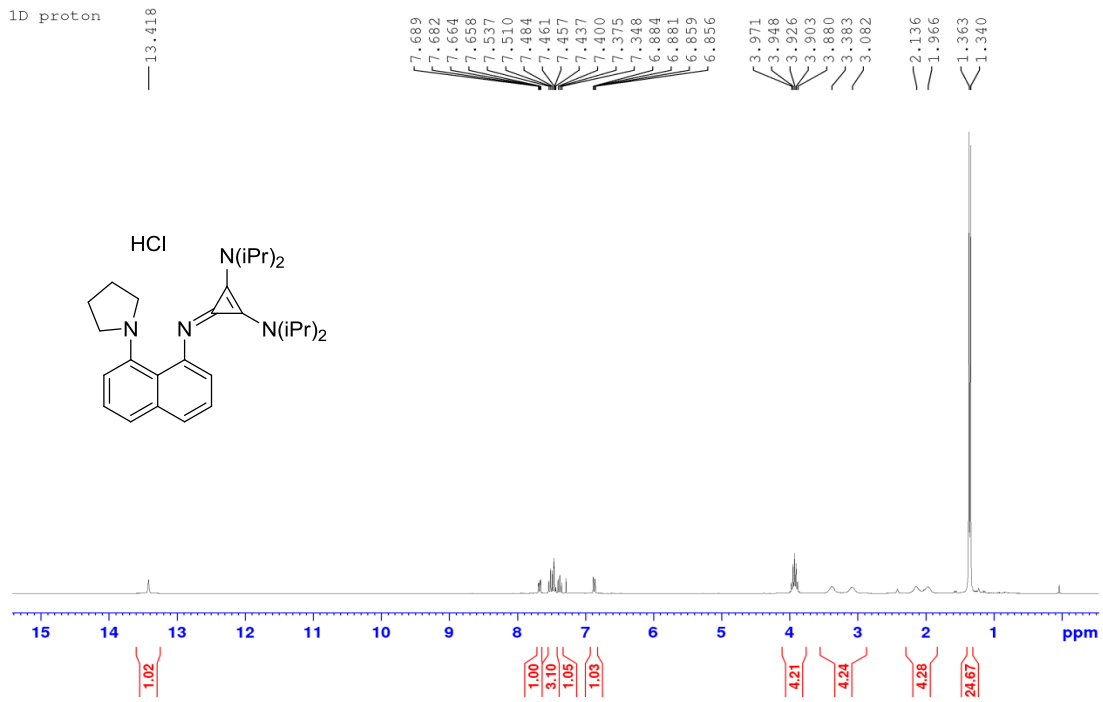
^{1}H NMR spectrum of **118** in $CDCl_3$



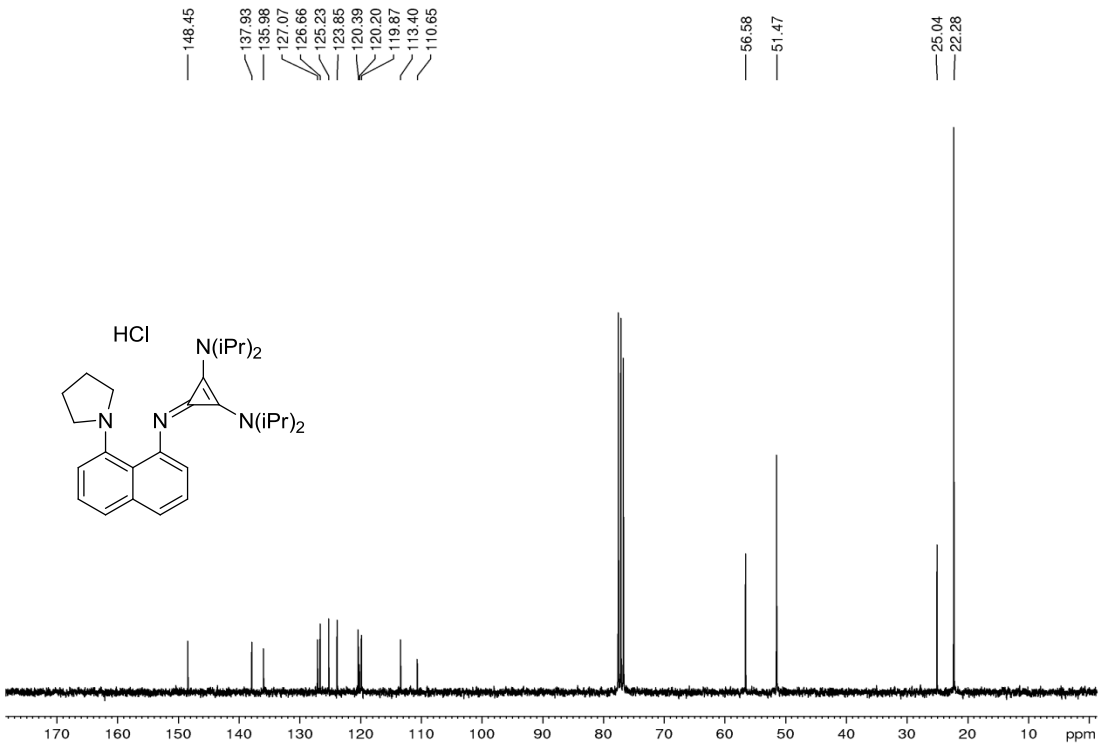
^{13}C NMR spectrum of **118** in $CDCl_3$



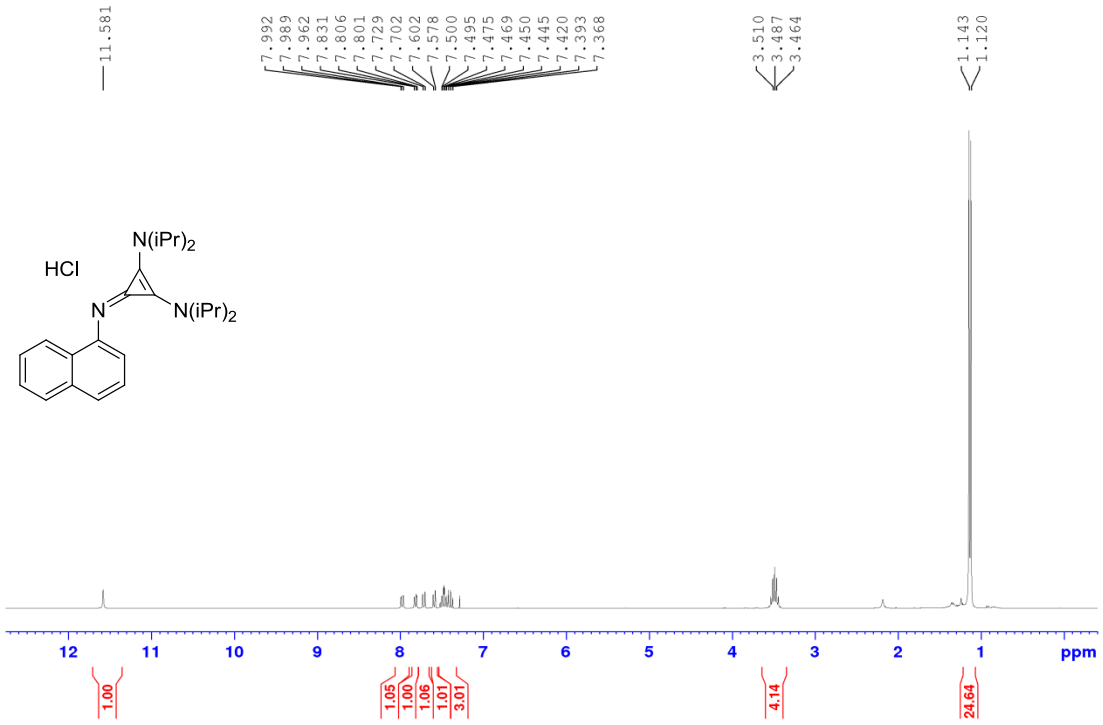
^{1}H NMR spectrum of **113** in $CDCl_3$



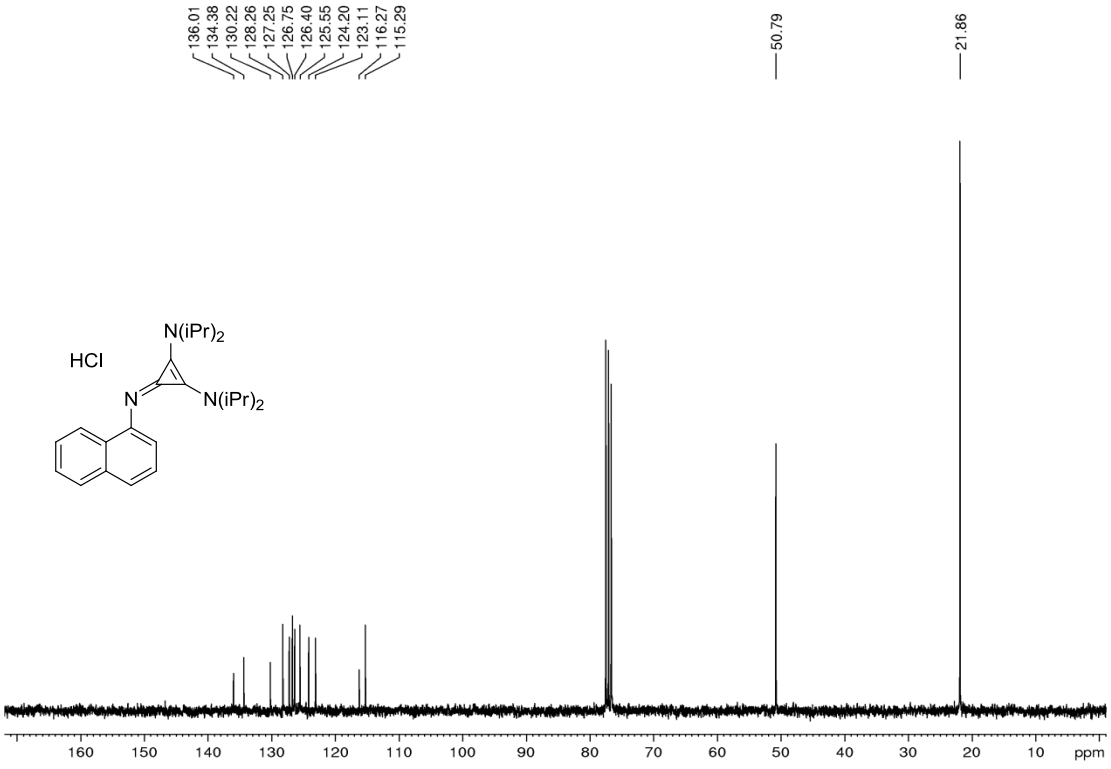
^{13}C NMR spectrum of **113** in $CDCl_3$



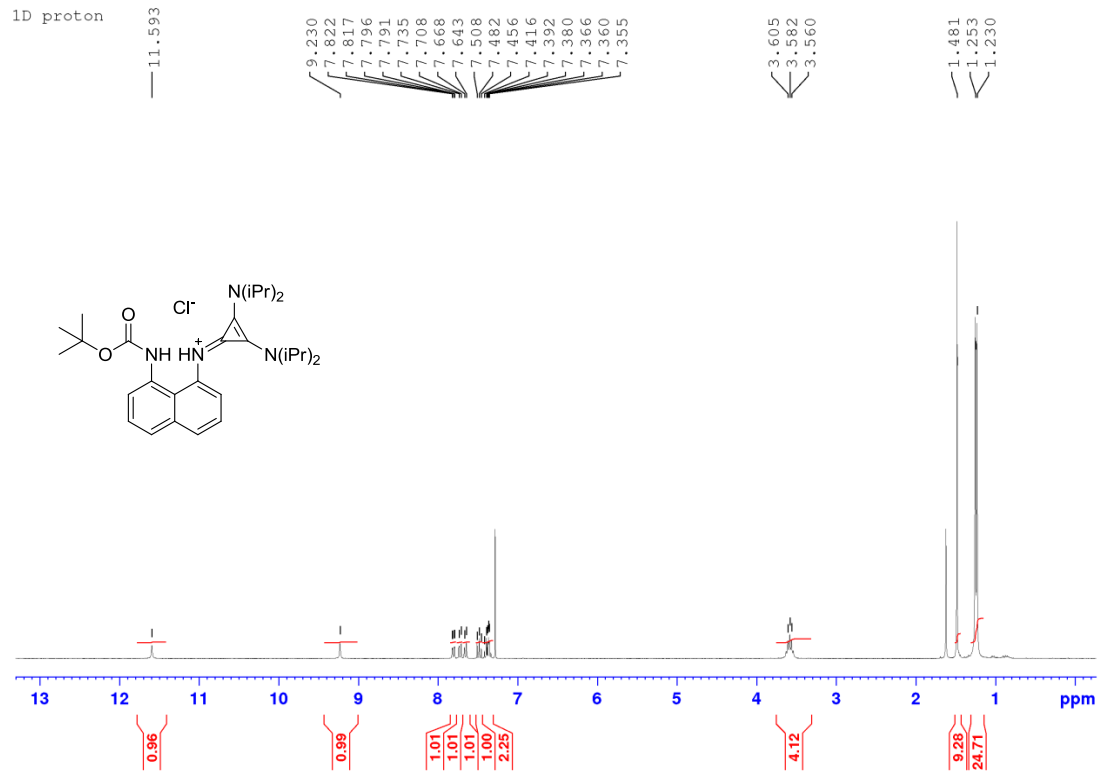
^{1}H NMR spectrum of **114** in $CDCl_3$



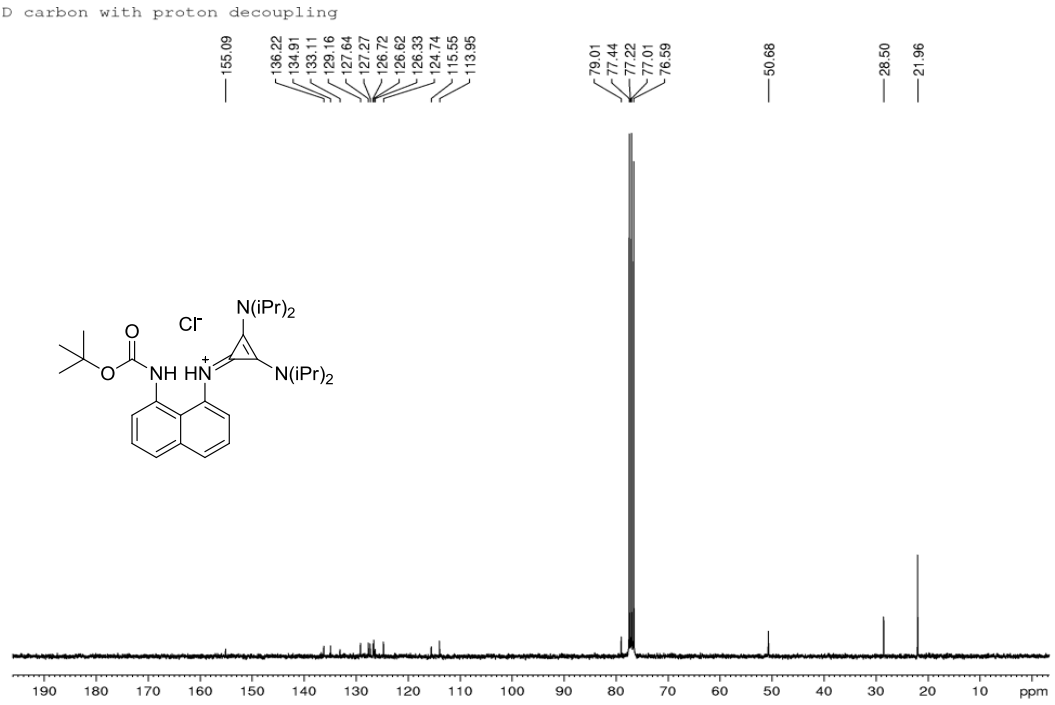
^{1}H NMR spectrum of **114** in $CDCl_3$



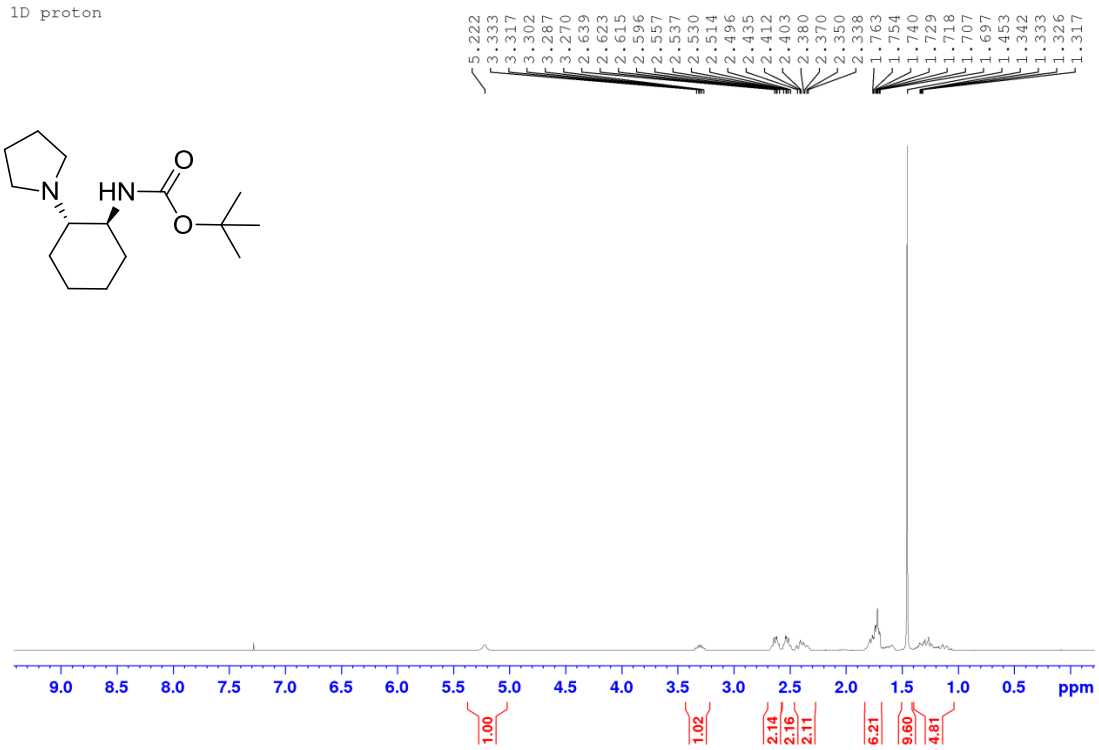
^{1}H NMR spectrum of **115** in $CDCl_3$



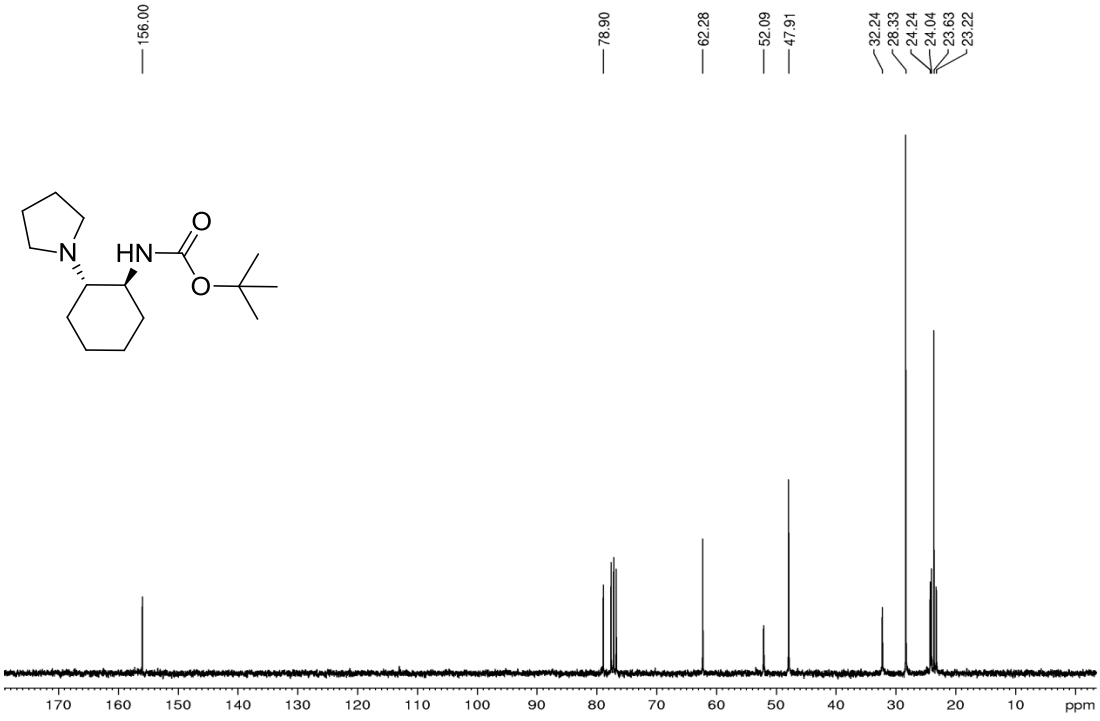
^{13}C NMR spectrum of **115** in $CDCl_3$



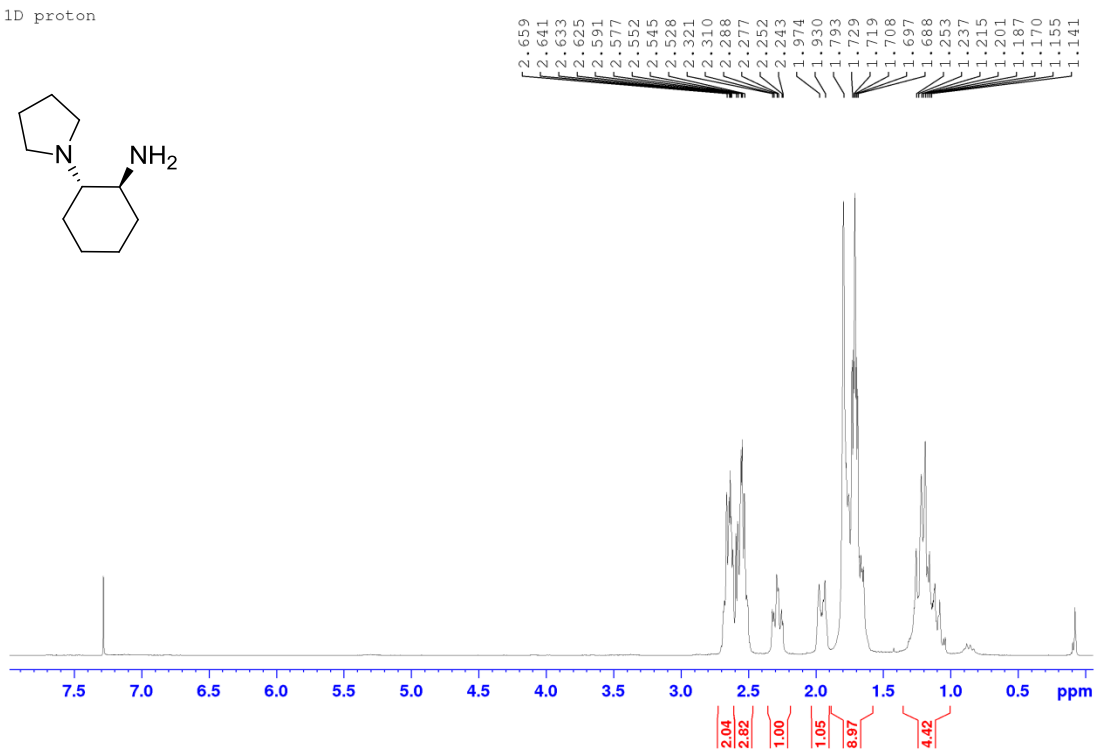
^{1}H NMR spectrum of **123** in $CDCl_3$



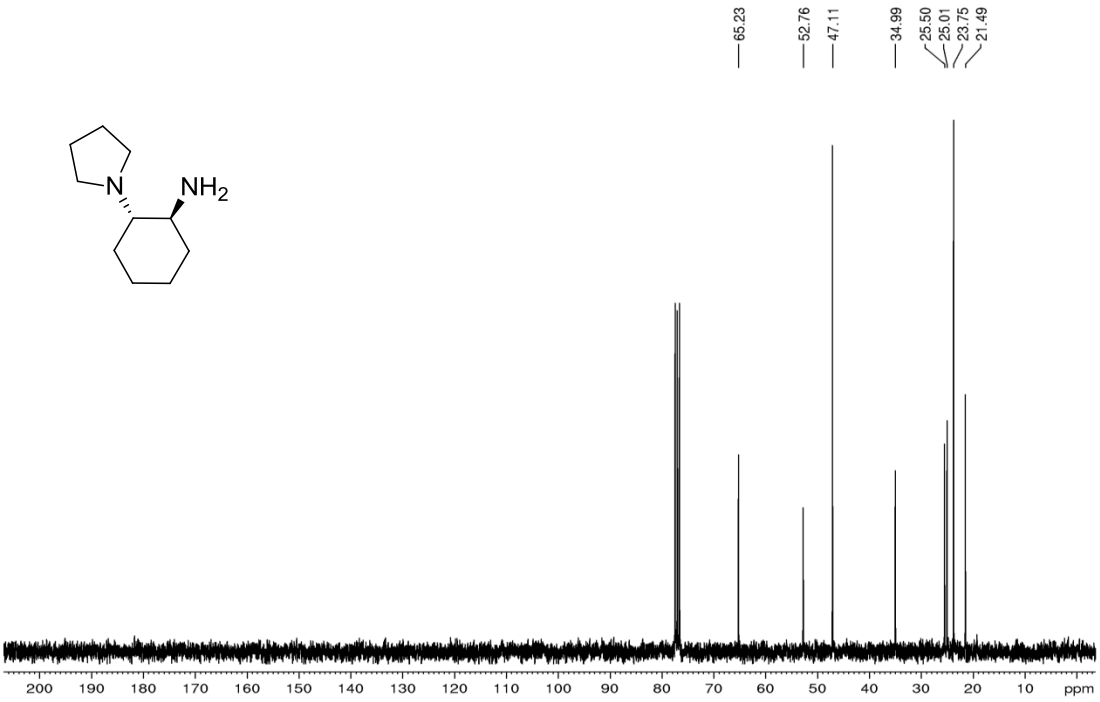
^{13}C NMR spectrum of **123** in $CDCl_3$



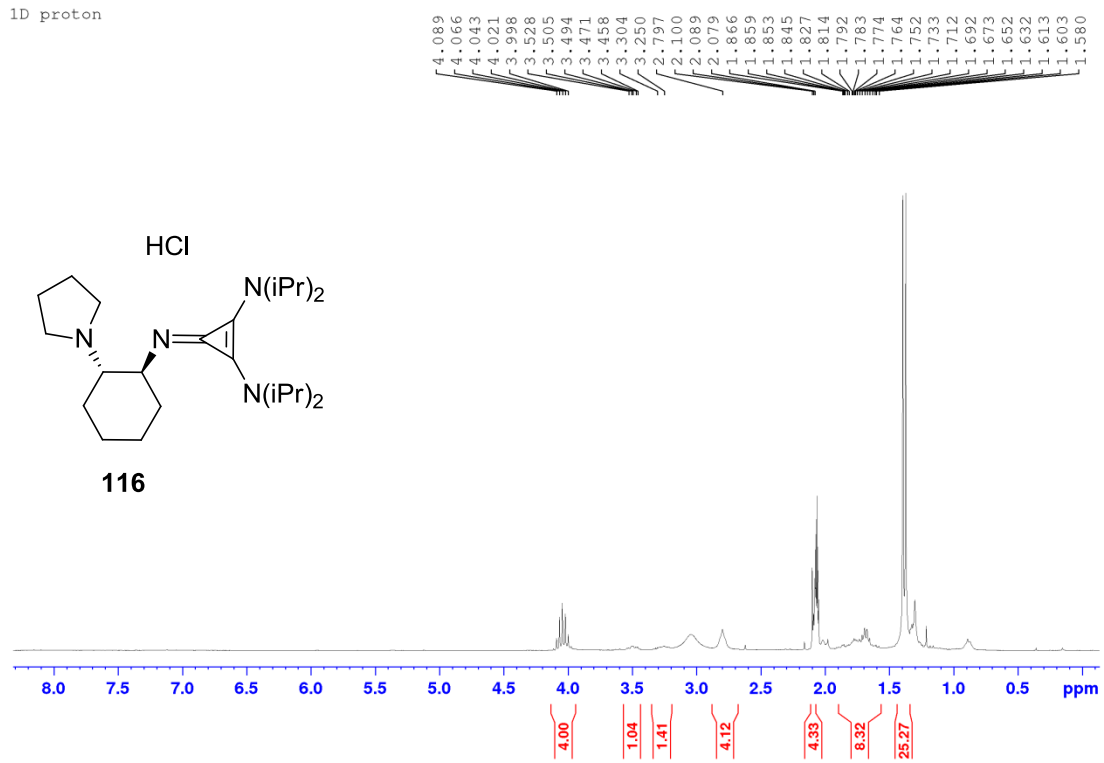
^{1}H NMR spectrum of **124** in $CDCl_3$



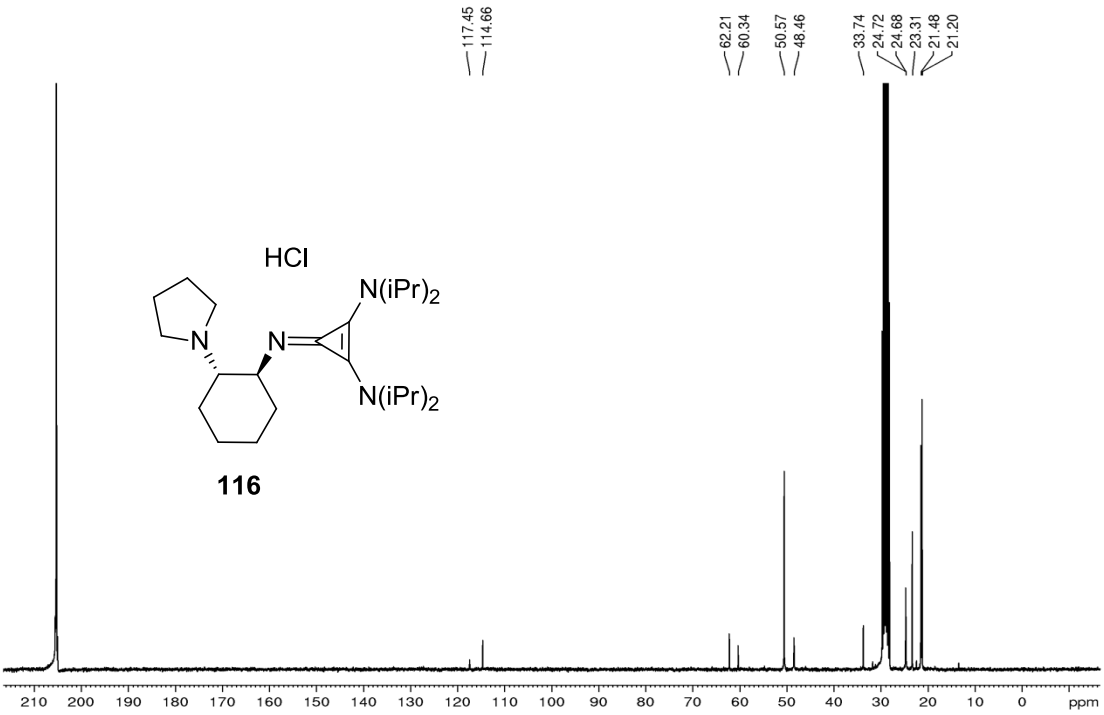
^{13}C NMR spectrum of **124** in $CDCl_3$



^{1}H NMR spectrum of **115** in $CO(CD_3)_2$

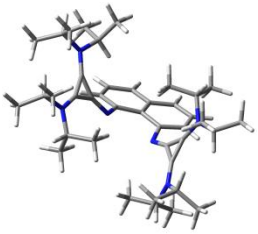


^{13}C NMR spectrum of **115** in $CO(CD_3)_2$



DFT calculated geometries and thermochemical data

89 (DACN)



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opt=calcfc freq=noraman b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=acetonitrile,smd)

- Thermochemistry -

Zero-point correction= 0.953221 (Hartree/Particle)
Thermal correction to Energy= 1.006493
Thermal correction to Enthalpy= 1.007437
Thermal correction to Gibbs Free Energy= 0.864434
Sum of electronic and zero-point Energies= -1889.147740
Sum of electronic and thermal Energies= -1889.094468
Sum of electronic and thermal Enthalpies= -1889.093524
Sum of electronic and thermal Free Energies= -1889.236526

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N	-4.32441700	0.28917100	0.88897700	C	2.29002800	2.83246300	2.74359200
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C	-0.62022400	4.12165000	-1.67207200	C	-1.50426300	-3.33682000	-1.29028000
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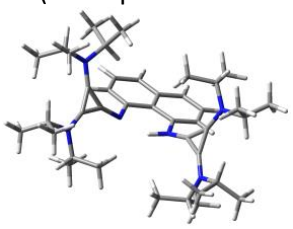
91 (Monoprotonated DACN)



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- Thermochemistry -

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Thermal correction to Enthalpy= 1.022027
Thermal correction to Gibbs Free Energy= 0.881422
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C	2.52909100	-2.34942600	-1.92644200	H	2.27841000	1.63950200	-2.84537100
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C	-4.11944300	1.70445500	-2.97856900	H	-1.53797100	2.23622900	-2.05477400
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H	3.46393200	-1.81561800	-1.78928100	H	2.04372400	-1.51334300	3.13624100
H	1.39928500	-5.37357700	-3.02218800	H	-5.00769800	4.57223800	1.54363000
H	-3.34151900	-2.10507900	-1.73761800	H	-3.33547700	4.10057100	1.19405600
H	-3.20778800	-4.43063900	-2.58114900	H	-4.35166600	4.81417700	-0.07790400
H	3.51814100	-4.14112800	-2.60069600	H	3.83828300	-4.26494200	1.27761900
H	4.81977900	2.49247300	1.10254600	H	5.18778000	-3.32662600	1.91981000
H	-0.99458200	-5.46993500	-3.01594600	H	4.75688700	-3.19726600	0.20214300
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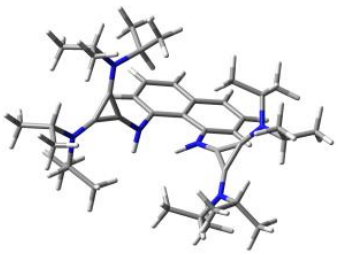
90 (Bis-protonated DACN)



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opt=calcfc freq=noraman b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=acetonitrile,smd)

- Thermochemistry -

Zero-point correction= 0.983104 (Hartree/Particle)

Thermal correction to Energy= 1.036332

Thermal correction to Enthalpy= 1.037276

Thermal correction to Gibbs Free Energy= 0.896636

Sum of electronic and zero-point Energies= -1890.098394

Sum of electronic and thermal Energies= -1890.045167

Sum of electronic and thermal Enthalpies= -1890.044223

Sum of electronic and thermal Free Energies= -1890.184863

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N	-1.25120500	-0.45020100	-1.09959700	C	-5.23050300	0.68910600	3.16250300
N	3.97309900	2.07839000	-0.33079700	C	-2.92240000	2.34270200	-3.03259700
N	3.23919400	-0.99880900	1.76000300	C	6.30160100	2.80158600	0.22130300
N	1.54969500	-0.43680600	-1.44869700	C	2.37190100	3.24479300	-1.86919700
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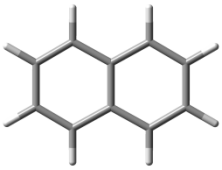
C	2.51389200	-2.59800700	-1.95569700	C	3.85109700	0.46089000	3.70030300
C	0.06639200	-2.41210300	-1.89199700	C	-1.22159800	3.42949900	-1.47829700
C	1.20378800	-4.52210500	-2.54449700	C	-6.57240600	-0.93959200	1.73850300
C	-2.38590800	-2.40359900	-1.91899700	C	-2.70109900	3.14600100	-1.74849700
C	0.00719000	-3.78430300	-2.33889700	C	-5.61309800	3.56550600	-0.54839700
C	-2.33490400	0.09370100	-0.49199700	C	4.29010300	4.07009000	1.13670300
C	2.44959600	-0.02570700	-0.51449700	C	1.55169200	-2.23670600	3.12880300
C	-2.41491000	-3.73239900	-2.38539700	C	-3.69659600	4.54950300	0.81080300
C	-1.19410700	-1.75450100	-1.63569700	C	3.25089000	-3.49850900	1.71480300
C	2.43558900	-3.95150700	-2.33829700	H	-0.48900400	0.18109800	-1.31439700
C	-3.09940200	1.23050200	-0.29099700	H	1.53169600	0.15929400	-2.27389700
C	3.34649800	0.93279100	-0.08529700	H	3.48419200	-2.12340900	-1.85019700
C	-3.37720400	0.04300200	0.42510300	H	1.11888700	-5.55440500	-2.87129700
C	4.84640000	2.71348900	0.69270300	H	-3.31970700	-1.87029800	-1.77979700
C	3.07739600	-0.21130800	0.70210300	H	-3.37231100	-4.20199800	-2.58899700
C	-1.24181100	-4.41830100	-2.57669700	H	3.34678800	-4.51920900	-2.49799700
C	-5.39940400	0.04410600	1.78300300	H	4.81189900	2.04238900	1.54900300
C	-4.33229900	3.27780400	0.24030300	H	-1.24331300	-5.44830100	-2.91949700
C	4.24249500	-0.73861000	2.83130300	H	-5.61160300	0.82800600	1.05390300
C	-3.64490700	-1.81789700	2.02230300	H	-4.58160000	2.63380400	1.08390300
C	-2.18060700	-1.68440000	2.44530300	H	4.19189300	-1.62611000	3.46490300
C	4.30079900	1.86189000	-2.80189700	H	-4.24530700	-1.85269600	2.93380300
C	-3.91190900	-3.10399700	1.23700300	H	-1.90740800	-2.54390000	3.06480300

H	-1.50420700	-1.66610100	1.58550300	H	2.87199600	0.30239200	4.16160300
H	-2.02270500	-0.77610000	3.03470300	H	3.80629800	1.39049000	3.12710300
H	5.33289900	1.54178800	-2.63149700	H	-1.09219700	4.04399900	-0.58329700
H	3.67949800	0.96939100	-2.92869700	H	-0.65730000	2.50239800	-1.34239700
H	4.26740000	2.42449000	-3.74019700	H	-0.78739700	3.96519800	-2.32829700
H	-3.69611100	-3.96869700	1.87370300	H	-6.69400600	-1.36609200	0.73870300
H	-4.95560900	-3.16969500	0.91890300	H	-7.49170500	-0.40289100	1.99330300
H	-3.27610900	-3.16989800	0.35140300	H	-6.45790700	-1.75599200	2.45780300
H	6.37789500	-0.56401400	3.09830300	H	-3.21779700	4.10110200	-1.86089700
H	5.91109300	-1.58651300	1.72820300	H	-6.06910000	2.63960700	-0.91179700
H	5.80929600	0.17678700	1.59840300	H	-6.33669700	4.07080700	0.09920300
H	1.72219200	-2.18520600	0.99970300	H	-5.42389700	4.21880600	-1.40639700
H	-6.14880200	1.21950700	3.43450300	H	3.26330300	3.97429100	1.50250300
H	-5.03640400	-0.05639500	3.94020300	H	4.90640300	4.46568900	1.95050300
H	-4.40740200	1.41050400	3.16270300	H	4.30340400	4.80459000	0.32500300
H	-3.98650000	2.14910300	-3.19829700	H	0.88419100	-3.10400500	3.11300300
H	-2.54199900	2.91160100	-3.88669700	H	2.16549200	-2.31220700	4.03200300
H	-2.39350200	1.38460100	-3.01149700	H	0.93879400	-1.33340500	3.19870300
H	6.68329900	1.81818600	-0.06879700	H	-4.41489600	5.03710400	1.47750300
H	6.92350100	3.18078500	1.03840300	H	-2.79899700	4.31680100	1.39110300
H	6.42090200	3.48388600	-0.62639700	H	-3.43289500	5.26830300	0.02900300
H	2.04910200	3.88139300	-1.04069700	H	2.59558900	-4.37520700	1.69090300
H	1.66160000	2.41929400	-1.96669700	H	3.93919000	-3.62401000	2.55700300
H	2.32180200	3.83179300	-2.79179700	H	3.83289000	-3.48401000	0.78890300
H	4.45300200	3.62298900	-1.60599700				
H	4.58629700	0.59408900	4.50040300				

96 (Naphthalene)



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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

- Thermochemistry -

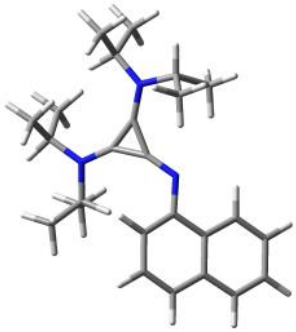
Zero-point correction= 0.147639 (Hartree/Particle)
Thermal correction to Energy= 0.154440
Thermal correction to Enthalpy= 0.155385
Thermal correction to Gibbs Free Energy= 0.116445
Sum of electronic and zero-point Energies= -385.757748
Sum of electronic and thermal Energies= -385.750946
Sum of electronic and thermal Enthalpies= -385.750002
Sum of electronic and thermal Free Energies= -385.788942

0 1

C	2.43310900	-0.70836200	-0.00000400	C	1.24466100	-1.40247700	-0.00001300

C	0.00002000	-0.71682200	-0.00000600	H	3.37732200	1.24501800	0.00002100
C	0.00002200	0.71683000	-0.00000300	C	-2.43309200	0.70836900	-0.00002000
C	1.24468300	1.40247400	0.00001500	C	-2.43312500	-0.70833400	0.00001800
C	2.43311300	0.70832600	0.00001300	H	-1.24207500	2.48950700	-0.00000600
H	3.37730800	-1.24506900	-0.00002400	H	-3.37728600	1.24508800	-0.00001500
C	-1.24472300	-1.40249600	0.00001200	H	-3.37734300	-1.24500700	0.00004400
C	-1.24465400	1.40248100	-0.00001700	H	1.24204900	-2.48950300	-0.00006600
H	1.24211700	2.48949900	0.00002500	H	-1.24217200	-2.48946900	0.00004600

97



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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

- Thermochemistry -

Zero-point correction= 0.552056 (Hartree/Particle)
Thermal correction to Energy= 0.582117
Thermal correction to Enthalpy= 0.583061
Thermal correction to Gibbs Free Energy= 0.490631
Sum of electronic and zero-point Energies= -1137.435354
Sum of electronic and thermal Energies= -1137.405293
Sum of electronic and thermal Enthalpies= -1137.404348
Sum of electronic and thermal Free Energies= -1137.496779

0 1

C	4.52627500	-2.15982000	1.55515300	N	0.93609600	-1.00438900	-0.33836200
C	3.34965700	-1.77027600	0.95241000	C	-0.21099700	-0.40426000	-0.21862900
C	3.32525800	-0.70860200	0.01262000	C	-1.59970100	-0.59431400	-0.10359000
C	4.55115900	-0.03738400	-0.30519500	C	-1.09259600	0.68624900	0.00788200
C	5.74613300	-0.46407100	0.33585800	N	-2.58784000	-1.51620700	-0.15504100
C	5.73761100	-1.49874100	1.24413300	N	-1.21716800	2.02329600	0.19943500
H	4.52684500	-2.97696500	2.27129600	C	-2.20040500	-2.92932800	-0.40050000
C	2.09634900	-0.28828800	-0.61687300	C	-3.99696600	-1.17632500	0.10471500
C	4.54652500	1.02941600	-1.24441900	C	-2.52740900	2.68394200	0.34873600
H	6.67541900	0.04553800	0.09255000	C	0.02060300	2.81833600	0.39685100
H	6.66192500	-1.81083300	1.72284500	C	-1.30915000	-3.48240000	0.72093800
C	3.36787300	1.40603000	-1.84724600	H	-1.77976100	-3.35215600	1.70026700
C	2.15384700	0.75264600	-1.54267400	H	-1.13516000	-4.55242800	0.56511900
H	5.48122500	1.52954600	-1.48274400	H	-0.33799100	-2.97871000	0.72160800
H	3.36489400	2.20981200	-2.57951800	C	-1.54604000	-3.10414500	-1.77791100
H	1.24577900	1.03602400	-2.06768600	H	-1.37639200	-4.16738400	-1.97782900

H	-2.18512500	-2.70428500	-2.57116800	H	-4.34502800	3.04167900	-0.79227600
H	-0.57695800	-2.59761500	-1.81084200	H	-2.87568200	2.93299700	-1.78153700
C	-4.52209400	-1.81861300	1.39831400	C	0.17443700	3.90986000	-0.67023000
H	-4.54537300	-2.91077700	1.32723300	H	1.14486900	4.40317100	-0.55757800
H	-3.89287900	-1.54743700	2.25100900	H	0.12694400	3.47968400	-1.67426500
H	-5.54345900	-1.48035700	1.60212300	H	-0.59724400	4.68356000	-0.58882700
C	-4.89754400	-1.48984300	-1.10007800	C	0.12516600	3.38537900	1.81993100
H	-5.91827600	-1.14343500	-0.90791100	H	-0.65856300	4.12205200	2.02893500
H	-4.52895200	-0.99263200	-2.00194600	H	0.05754900	2.58715900	2.56464600
H	-4.94893600	-2.56452100	-1.30171500	H	1.08871800	3.88836000	1.94917700
C	-3.25004800	2.28117000	1.64496600	H	0.83942900	2.11006100	0.25691500
H	-4.21247000	2.79763500	1.72279200	H	-2.29863800	3.75028700	0.43368800
H	-3.44084700	1.20629000	1.69045000	H	-4.01137700	-0.09465000	0.24682300
H	-2.64916300	2.54503500	2.51910700	H	-3.14254400	-3.48572400	-0.39550700
C	-3.39065000	2.51855400	-0.91037500	H	2.41315200	-2.26764100	1.17778000
H	-3.60730300	1.46872200	-1.12393800				

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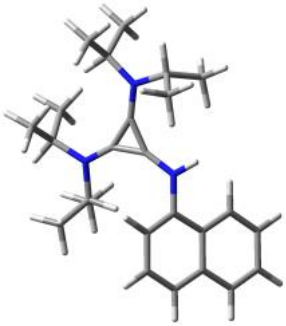

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

- Thermochemistry -

Zero-point correction= 0.565756 (Hartree/Particle)
Thermal correction to Energy= 0.596243
Thermal correction to Enthalpy= 0.597187
Thermal correction to Gibbs Free Energy= 0.503725
Sum of electronic and zero-point Energies= -1137.856726
Sum of electronic and thermal Energies= -1137.826239
Sum of electronic and thermal Enthalpies= -1137.825295
Sum of electronic and thermal Free Energies= -1137.918757

1 1

C	-4.34845100	-1.98459500	-1.88115700	C	-2.10916100	-0.50762700	0.74835700
C	-3.20502200	-1.69399400	-1.17059400	C	-4.56803100	0.63964300	1.43782600
C	-3.25285700	-0.83203600	-0.04294100	H	-6.61765300	-0.13434300	-0.13659300
C	-4.50986300	-0.24961600	0.33158000	H	-6.48433300	-1.66538600	-2.07239500
C	-5.66721100	-0.57322300	-0.42586900	C	-3.43947900	0.93924500	2.16537600
C	-5.59188600	-1.42485300	-1.50374200	C	-2.20179700	0.34498100	1.82937100
H	-4.29659300	-2.64411100	-2.74177900	H	-5.52526200	1.07735500	1.70528400

H	-3.49541100	1.60917400	3.01696000	H	5.26052800	-2.02479200	1.24879600
H	-1.32258700	0.53767000	2.43676800	C	2.90363400	2.52194200	-1.73585500
N	-0.85353200	-1.12660700	0.43326600	H	3.77113300	3.17766500	-1.85346900
C	0.30811200	-0.48131500	0.24167800	H	3.25732600	1.48904600	-1.79141200
C	1.68292800	-0.55846400	0.10266000	H	2.23421200	2.68968600	-2.58316000
C	1.02071700	0.67927300	-0.02127100	C	3.10642100	2.77364700	0.81992500
N	2.75762000	-1.34674000	0.10463800	H	3.50207600	1.77167600	1.00569700
N	0.97232700	1.99364900	-0.22735000	H	3.95883000	3.44403300	0.67863800
C	2.58402200	-2.80119100	0.38916300	H	2.56757600	3.09323000	1.71584700
C	4.11860400	-0.81854300	-0.18474500	C	-0.57450600	3.65585400	0.82404300
C	2.19361900	2.82607200	-0.41050400	H	-1.59682900	4.04277900	0.78859400
C	-0.36939900	2.65179200	-0.31522200	H	-0.42393400	3.18425400	1.79903100
C	1.78196300	-3.50428800	-0.71304800	H	0.10065300	4.51365600	0.74674100
H	2.24705200	-3.36320000	-1.69182500	C	-0.60297900	3.27222500	-1.69739900
H	1.73000200	-4.57780200	-0.51105100	H	0.07105300	4.11154800	-1.89463400
H	0.75430700	-3.13097000	-0.77803500	H	-0.47811300	2.53084900	-2.49134200
C	2.02048100	-3.04304400	1.79423200	H	-1.62496600	3.65785500	-1.75267500
H	1.99459400	-4.11598400	2.00428600	H	-1.09200500	1.84421400	-0.18299500
H	2.64112300	-2.56194900	2.55453600	H	1.81275700	3.84730100	-0.47833600
H	1.00003400	-2.66148700	1.90276300	H	3.97580400	0.24824300	-0.35943600
C	4.70163300	-1.42950300	-1.46463800	H	3.59691400	-3.20878800	0.36843700
H	4.88909800	-2.50245300	-1.35958400	H	-2.25476800	-2.11433600	-1.48320700
H	4.03341700	-1.27799400	-2.31718700	H	-0.81232300	-2.13708300	0.46216300
H	5.65987800	-0.95464100	-1.69411900				
C	5.05125600	-0.97485800	1.02252300				
H	6.00976400	-0.49270300	0.81035000				
H	4.62525700	-0.50946600	1.91597500				

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.624512 (Hartree/Particle)
Thermal correction to Energy= 0.658769
Thermal correction to Enthalpy= 0.659713
Thermal correction to Gibbs Free Energy= 0.557923
Sum of electronic and zero-point Energies= -1271.318138
Sum of electronic and thermal Energies= -1271.283881
Sum of electronic and thermal Enthalpies= -1271.282937
Sum of electronic and thermal Free Energies= -1271.384727

0 1

C	-4.32082400	-0.81612500	-1.58884600	C	-1.76272400	0.33468100	2.42457300
C	-3.13996700	-0.99162800	-0.87971900	H	-4.93945400	1.52897300	2.56097000
C	-2.98088100	-0.35418700	0.41280000	H	-2.84519300	1.47794600	3.90352500
C	-4.11749600	0.37066200	0.93388700	H	-0.84259300	0.31613100	3.00056000
C	-5.31132600	0.48858800	0.17025400	N	-0.58178200	-0.98572600	0.82292800
C	-5.40158000	-0.07110200	-1.07668000	C	0.48688700	-0.33540600	0.50606600
H	-4.43389800	-1.29411400	-2.55462800	C	1.87793400	-0.42502900	0.27402200
C	-1.75865500	-0.31885300	1.19067800	C	1.25881900	0.78492500	0.06916000
C	-4.05545400	1.01222700	2.19799500	N	2.98459300	-1.20286100	0.33891900
H	-6.14125700	1.04850900	0.59254000	N	1.35686800	2.08933000	-0.29504900
H	-6.30885100	0.03040600	-1.66606800	C	2.87611600	-2.53041700	0.98777600
C	-2.89619100	0.98836700	2.93448800	C	4.24779900	-0.77887900	-0.29010700
				C	2.69232800	2.70482300	-0.41290200

C	0.16627900	2.82398000	-0.78969100	H	4.17214800	3.23617900	-1.92119500
C	1.94602400	-3.47458700	0.21318500	H	3.11570600	1.89029500	-2.39384400
H	2.26500700	-3.57713400	-0.82836300	C	-0.58919000	2.02888400	-1.86279700
H	1.95062400	-4.46921100	0.67205100	H	-1.42277400	2.62338200	-2.24970000
H	0.92050700	-3.09523000	0.23256600	H	0.07137300	1.77793000	-2.69880000
C	2.44267400	-2.39979600	2.45448100	H	-1.00091300	1.09985200	-1.46033400
H	2.46534000	-3.37961400	2.94286500	C	-0.75044300	3.27745200	0.35337400
H	3.10806700	-1.72663300	3.00356800	H	-1.17217000	2.42273400	0.88687500
H	1.41996400	-2.01614600	2.51876600	H	-0.20209300	3.89391000	1.07186900
C	4.67723100	-1.72002900	-1.42675400	H	-1.58125600	3.87103500	-0.04274600
H	4.92432500	-2.71968700	-1.05520300	H	0.56845800	3.72192400	-1.27044400
H	3.88185700	-1.81849700	-2.17076100	H	3.37205700	2.00746000	0.08552300
H	5.56893400	-1.32626600	-1.92568900	H	4.03042200	0.19238600	-0.74238100
C	5.36807100	-0.57810400	0.74185000	H	3.88839700	-2.94635400	0.96658400
H	6.26871500	-0.18686500	0.25712800	N	-2.09930300	-1.78615800	-1.43687100
H	5.05996600	0.12713500	1.51931000	C	-2.07050300	-1.91092600	-2.88483800
H	5.64076800	-1.52056200	1.22801400	H	-1.09972600	-2.32620100	-3.17746500
C	2.78226000	4.03394000	0.35147500	H	-2.84812400	-2.57876900	-3.30121900
H	3.80913400	4.41325200	0.32348500	H	-2.17861600	-0.92795300	-3.35023800
H	2.13806100	4.80263400	-0.08687100	C	-1.92334800	-3.08699300	-0.79121700
H	2.49246200	3.89978000	1.39709100	H	-0.98791700	-3.53839600	-1.13732000
C	3.14730900	2.85278800	-1.87425200	H	-1.85488000	-2.96699800	0.28783500
H	2.50936000	3.55301100	-2.42338000	H	-2.75146500	-3.77786700	-1.03352300

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.638627 (Hartree/Particle)
Thermal correction to Energy= 0.672981
Thermal correction to Enthalpy= 0.673925
Thermal correction to Gibbs Free Energy= 0.571731
Sum of electronic and zero-point Energies= -1271.752049
Sum of electronic and thermal Energies= -1271.717696
Sum of electronic and thermal Enthalpies= -1271.716752
Sum of electronic and thermal Free Energies= -1271.818946

1 1

C	-4.88154300	1.01431300	0.96248500	H	-2.41803900	-3.18337800	-2.76337800
C	-3.57640400	0.88983400	0.52763700	H	-0.62050100	-1.60113600	-2.09626100
C	-3.19331600	-0.21911900	-0.29795400	N	-2.59799300	1.91803200	0.87823100
C	-4.22006100	-1.14541900	-0.69694400	N	-0.82092800	0.39348100	-0.38053300
C	-5.54631600	-0.97233800	-0.22223500	C	0.48422900	0.09359500	-0.26324100
C	-5.87215900	0.07904500	0.59924100	C	1.75391300	0.64663600	-0.23593200
H	-5.15674300	1.85894400	1.58648400	C	1.57305600	-0.73051300	0.03134300
C	-1.86082700	-0.47276500	-0.78069000	N	2.43237500	1.78101500	-0.40164900
C	-3.91239100	-2.22260900	-1.57154300	N	2.08253000	-1.91616100	0.36327400
H	-6.30324600	-1.68765000	-0.52955400	C	1.65471800	2.96660600	-0.88366200
H	-6.88847800	0.20576100	0.95772000	C	3.88107000	1.95013600	-0.10320300
C	-2.64165000	-2.38288300	-2.06556400	C	3.56081900	-2.11579700	0.34708800
C	-1.61518300	-1.49740800	-1.67502500	C	1.22418600	-3.02528000	0.89012300
H	-4.70813000	-2.90285000	-1.85820600	H	-1.20237600	1.25738300	0.07012300
				C	1.53829000	4.04020400	0.20522300

H	0.88951400	4.84910700	-0.14364900	H	3.87753400	-3.33628400	2.14731500
H	1.11005400	3.62814300	1.12392500	C	0.18786400	-2.51423500	1.89549400
H	2.50683700	4.48677500	0.45007800	H	-0.31137800	-3.36736600	2.36285700
C	2.21666800	3.51984300	-2.19771000	H	0.65893400	-1.92314300	2.68630800
H	1.56408100	4.31767700	-2.56378900	H	-0.58565400	-1.90977000	1.41443900
H	3.21465100	3.95016900	-2.07144800	C	0.59508500	-3.88385900	-0.21227200
H	2.26592000	2.74334200	-2.96572200	H	-0.19299800	-3.34332400	-0.73785800
C	4.77188000	1.30169000	-1.17078500	H	1.33799100	-4.21743700	-0.93974500
H	5.82444600	1.49840800	-0.94703200	H	0.14201300	-4.77238400	0.23852200
H	4.63956000	0.21764300	-1.21916200	H	1.92604400	-3.65686800	1.43963200
H	4.55398900	1.70692300	-2.16168800	H	3.96228100	-1.17301200	-0.02552700
C	4.22054100	1.52904200	1.32955900	H	4.04282800	3.02906500	-0.16331900
H	3.61137800	2.07967700	2.05165500	H	0.65311500	2.58121800	-1.09227400
H	4.06189300	0.46143100	1.49489500	C	-2.31522700	1.95888000	2.32381300
H	5.27240700	1.74217000	1.53910600	H	-3.18706300	2.26157200	2.92068600
C	3.97995800	-3.21852900	-0.63188200	H	-1.99540300	0.96958900	2.65990200
H	3.59002600	-3.02970800	-1.63572900	H	-1.50811900	2.67375900	2.51280800
H	5.07179300	-3.25696800	-0.69098100	C	-2.95751000	3.24700600	0.35074500
H	3.63715300	-4.20423800	-0.30456900	H	-3.85632100	3.66875000	0.82210800
C	4.13368400	-2.34912200	1.75245500	H	-2.12629100	3.93687500	0.52798800
H	5.22548400	-2.29537700	1.71077000	H	-3.13333300	3.17594300	-0.72487000
H	3.78201500	-1.59572500	2.46280500				

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H	-1.79676700	2.60601600	3.10349800	H	-4.60602100	-1.35897400	1.02315400
H	-1.54425100	0.99867500	2.40956400	H	-3.21659900	-2.02209200	1.90837800
C	-2.81720600	2.72933000	0.54857100	H	-3.21944100	-0.32619200	1.40827700
H	-2.90704200	3.15091000	-0.45777500	C	-3.22690300	-0.78078300	-1.35004000
H	-3.28704100	1.74264500	0.54389600	H	-2.75841500	-1.09439200	-2.28918500
H	-3.38521500	3.37148100	1.23127300	H	-4.31261700	-0.76522700	-1.50108700
H	3.35994100	-2.34739100	0.06436400	H	-2.90181000	0.24160500	-1.13755700
H	2.60558800	1.13390800	0.43475300	C	-3.29208200	-3.16926200	-0.58652300
H	-0.76808500	3.54128800	-1.30245700	H	-2.80915700	-3.49234700	-1.51413700
H	-0.96433600	3.67366700	1.04557000	H	-3.00760600	-3.87492400	0.19993100
C	-2.83512400	-1.74692500	-0.21453300	H	-4.37828800	-3.21736700	-0.72423000
C	-3.51302800	-1.33664200	1.10806000				

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.638627 (Hartree/Particle)
Thermal correction to Energy= 0.672981
Thermal correction to Enthalpy= 0.673925
Thermal correction to Gibbs Free Energy= 0.571731
Sum of electronic and zero-point Energies= -1271.752049
Sum of electronic and thermal Energies= -1271.717696
Sum of electronic and thermal Enthalpies= -1271.716752
Sum of electronic and thermal Free Energies= -1271.818946

1 1

C	-4.88154300	1.01431300	0.96248500	H	-1.20237600	1.25738300	0.07012300
C	-3.57640400	0.88983400	0.52763700	C	1.53829000	4.04020400	0.20522300
C	-3.19331600	-0.21911900	-0.29795400	H	0.88951400	4.84910700	-0.14364900
C	-4.22006100	-1.14541900	-0.69694400	H	1.11005400	3.62814300	1.12392500
C	-5.54631600	-0.97233800	-0.22223500	H	2.50683700	4.48677500	0.45007800
C	-5.87215900	0.07904500	0.59924100	C	2.21666800	3.51984300	-2.19771000
H	-5.15674300	1.85894400	1.58648400	H	1.56408100	4.31767700	-2.56378900
C	-1.86082700	-0.47276500	-0.78069000	H	3.21465100	3.95016900	-2.07144800
C	-3.91239100	-2.22260900	-1.57154300	H	2.26592000	2.74334200	-2.96572200
H	-6.30324600	-1.68765000	-0.52955400	C	4.77188000	1.30169000	-1.17078500
H	-6.88847800	0.20576100	0.95772000	H	5.82444600	1.49840800	-0.94703200
C	-2.64165000	-2.38288300	-2.06556400	H	4.63956000	0.21764300	-1.21916200
C	-1.61518300	-1.49740800	-1.67502500	H	4.55398900	1.70692300	-2.16168800
H	-4.70813000	-2.90285000	-1.85820600	C	4.22054100	1.52904200	1.32955900
H	-2.41803900	-3.18337800	-2.76337800	H	3.61137800	2.07967700	2.05165500
H	-0.62050100	-1.60113600	-2.09626100	H	4.06189300	0.46143100	1.49489500
N	-2.59799300	1.91803200	0.87823100	H	5.27240700	1.74217000	1.53910600
N	-0.82092800	0.39348100	-0.38053300	C	3.97995800	-3.21852900	-0.63188200
C	0.48422900	0.09359500	-0.26324100	H	3.59002600	-3.02970800	-1.63572900
C	1.75391300	0.64663600	-0.23593200	H	5.07179300	-3.25696800	-0.69098100
C	1.57305600	-0.73051300	0.03134300	H	3.63715300	-4.20423800	-0.30456900
N	2.43237500	1.78101500	-0.40164900	C	4.13368400	-2.34912200	1.75245500
N	2.08253000	-1.91616100	0.36327400	H	5.22548400	-2.29537700	1.71077000
C	1.65471800	2.96660600	-0.88366200	H	3.78201500	-1.59572500	2.46280500
C	3.88107000	1.95013600	-0.10320300	H	3.87753400	-3.33628400	2.14731500
C	3.56081900	-2.11579700	0.34708800	C	0.18786400	-2.51423500	1.89549400
C	1.22418600	-3.02528000	0.89012300	H	-0.31137800	-3.36736600	2.36285700

H	0.65893400	-1.92314300	2.68630800	H	0.65311500	2.58121800	-1.09227400
H	-0.58565400	-1.90977000	1.41443900	C	-2.31522700	1.95888000	2.32381300
C	0.59508500	-3.88385900	-0.21227200	H	-3.18706300	2.26157200	2.92068600
H	-0.19299800	-3.34332400	-0.73785800	H	-1.99540300	0.96958900	2.65990200
H	1.33799100	-4.21743700	-0.93974500	H	-1.50811900	2.67375900	2.51280800
H	0.14201300	-4.77238400	0.23852200	C	-2.95751000	3.24700600	0.35074500
H	1.92604400	-3.65686800	1.43963200	H	-3.85632100	3.66875000	0.82210800
H	3.96228100	-1.17301200	-0.02552700	H	-2.12629100	3.93687500	0.52798800
H	4.04282800	3.02906500	-0.16331900				
H	-3.13333300	3.17594300	-0.72487000				

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.504749 (Hartree/Particle)
Thermal correction to Energy= 0.532344
Thermal correction to Enthalpy= 0.533288
Thermal correction to Gibbs Free Energy= 0.445571
Sum of electronic and zero-point Energies= -983.828701
Sum of electronic and thermal Energies= -983.801106
Sum of electronic and thermal Enthalpies= -983.800162
Sum of electronic and thermal Free Energies= -983.887879

0 1

N	-1.29052000	-1.55010300	-0.04134900	H	4.51991200	-1.14329800	1.50610900
C	-0.27638100	-0.75153600	-0.03366300	C	3.48536800	-0.12172300	-1.68228800
C	1.13447800	-0.71320500	-0.02332500	H	4.49177900	0.10715700	-2.04680600
C	0.44912600	0.48043700	-0.01385700	H	2.93189100	-0.61429900	-2.48665800
N	2.25142400	-1.48391900	0.02902400	H	2.98768400	0.82550300	-1.46542800
N	0.48818100	1.84052000	-0.03722400	C	1.41631200	-3.63685600	-0.94688100
C	1.71553200	2.52808900	0.41300500	H	1.98351000	-3.44449200	-1.86405000
C	-0.75575000	2.62847300	-0.20295600	H	1.38749500	-4.72059300	-0.78943200
C	3.57458300	-1.03172800	-0.45140800	H	0.38873600	-3.28486500	-1.08177800
C	2.06165200	-2.94086700	0.26066800	C	1.28420700	-3.21180000	1.55390000
C	-1.37475700	2.40282800	-1.58760400	H	1.74404300	-2.69267600	2.40064500
H	-2.23258000	3.06814200	-1.72942700	H	0.24231700	-2.89314200	1.45891700
H	-0.64521200	2.60499500	-2.37748400	H	1.28927600	-4.28598400	1.76673800
H	-1.73413300	1.37668700	-1.69658500	H	-0.42998300	3.67198300	-0.15538800
C	-1.77028800	2.40839600	0.92835200	H	2.47342000	1.74407300	0.46806500
H	-2.16195400	1.38912700	0.92590100	H	4.08091000	-1.94652300	-0.78038500
H	-1.32034800	2.60398400	1.90575700	H	3.07665600	-3.33290600	0.39280000
H	-2.61986500	3.08783400	0.80278800	C	-2.62192000	-1.11073500	-0.02880200
C	1.57814400	3.12793300	1.82209600	C	-3.30876800	-0.83106600	-1.22642800
H	0.84212500	3.93795600	1.84654900	C	-3.35256300	-1.06816600	1.17463700
H	1.27142900	2.36391800	2.54205500	C	-4.66058900	-0.48846700	-1.21466900
H	2.53631300	3.54444300	2.15102700	H	-2.76639900	-0.90481600	-2.16483500
C	2.20315900	3.57051300	-0.60379100	C	-4.70418700	-0.72570900	1.18076400
H	3.17660800	3.96637600	-0.29641000	H	-2.83933600	-1.31243500	2.10019800
H	2.30877100	3.12903700	-1.59871200	C	-5.36786800	-0.42944900	-0.01212100
H	1.51751400	4.42028300	-0.68157900	H	-5.16588100	-0.27342900	-2.15295900
C	4.42192600	-0.43129300	0.68119200	H	-5.24344700	-0.69422100	2.12422600
H	5.42686800	-0.18184000	0.32351400	H	-6.42156900	-0.16674500	-0.00538800
H	3.97135100	0.48086700	1.08393600				

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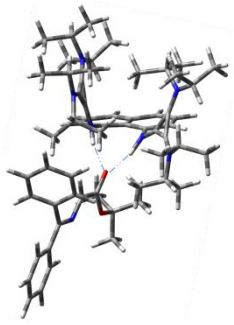

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opt=calcfc freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

Zero-point correction= 0.349480 (Hartree/Particle)
Thermal correction to Energy= 0.369633
Thermal correction to Enthalpy= 0.370577
Thermal correction to Gibbs Free Energy= 0.299469
Sum of electronic and zero-point Energies= -940.720026
Sum of electronic and thermal Energies= -940.699873
Sum of electronic and thermal Enthalpies= -940.698929
Sum of electronic and thermal Free Energies= -940.770037

-1 1

O	2.94168700	-2.24927000	0.16640100
C	2.26387700	-1.21556500	0.08701600
N	0.14797400	-0.05749500	-0.00172400
C	-1.15740200	0.07493500	-0.00873700
C	-2.09818300	-1.08436800	0.01018000
C	-3.06904900	-1.22525900	1.01197600
C	-2.02750200	-2.08170000	-0.97261600
C	-3.93759700	-2.31303300	1.02914000
H	-3.14205300	-0.46388600	1.78374500
C	-2.88822900	-3.17472800	-0.95616800
H	-1.28146600	-1.99418400	-1.75692200
C	-3.85005000	-3.29494000	0.04479200
H	-4.68195600	-2.39634200	1.81585700
H	-2.81257800	-3.93273000	-1.73041500
H	-4.52547700	-4.14496800	0.05760500
C	-1.69424500	1.44670200	-0.03901300
C	-3.05351700	1.72834500	-0.27207300
C	-0.83587500	2.55084100	0.14390600
C	-3.52741500	3.03689900	-0.31133700
H	-3.75026500	0.91157500	-0.43234100
C	-1.31021500	3.85338500	0.09831200
H	0.21539900	2.34747100	0.31784600
C	-2.66382500	4.11304100	-0.12688600
H	-4.58396800	3.21400700	-0.49476000
H	-0.61673200	4.67777300	0.24411300
H	-3.03546700	5.13273700	-0.15831900
O	2.83683200	0.02801900	0.00906900
C	4.26786000	0.19479200	0.00538800
C	0.83786500	-1.19857200	0.06276200
H	0.36602100	-2.18060100	0.12148000
C	4.88553100	-0.31585700	1.30986700
H	4.76577200	-1.39543500	1.39184200
H	5.95127900	-0.06636200	1.34031100
H	4.39765000	0.16072600	2.16601400
C	4.89403800	-0.48022000	-1.21791400
H	5.96117800	-0.24143800	-1.27217500
H	4.76853400	-1.56101300	-1.15980200
H	4.41414300	-0.11554400	-2.13160700
C	4.44208200	1.71087600	-0.09062100
H	3.97814000	2.09309500	-1.00415200
H	3.97399900	2.20339600	0.76663100
H	5.50499200	1.97074700	-0.10450800

90 (DCM)

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opt=calcfc freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

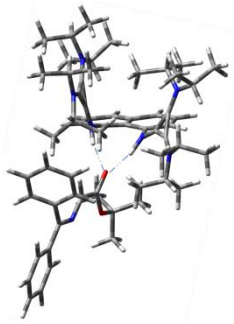
Zero-point correction= 1.002472 (Hartree/Particle)
Thermal correction to Energy= 1.053442
Thermal correction to Enthalpy= 1.054386
Thermal correction to Gibbs Free Energy= 0.922113
Sum of electronic and zero-point Energies= -1889.402764
Sum of electronic and thermal Energies= -1889.351795

Sum of electronic and thermal Enthalpies= -1889.350851
Sum of electronic and thermal Free Energies= -1889.483124

2 1

N	1.13027500	0.69788100	-1.25314600
H	0.17370300	0.40199600	-1.40966000
C	2.01249900	-0.22835000	-0.84830200
N	4.39692500	-0.45720300	0.26370900
C	3.19580200	-0.65537000	-0.27317900
N	1.75458900	-2.80663400	-0.81154400
C	2.22853500	-1.58011100	-0.67789400
N	-1.54176900	1.45842500	-1.33242200
H	-1.86696900	1.42311800	-2.29359300
C	-2.31684300	0.77123700	-0.45325600
N	-2.12505900	0.51304200	2.09834900
C	-2.51785900	0.38845600	0.84743700
N	-4.23318200	-0.94994200	-0.67410900
C	-3.30064000	-0.14991300	-0.19270200
C	1.39474900	2.07695800	-1.38030900
C	2.66109000	2.48775900	-1.71627800
H	3.39425600	1.74323900	-2.00907400
C	3.02436100	3.84903700	-1.65016800
H	4.03851300	4.14096000	-1.90169400
C	2.11287200	4.78002300	-1.23653100
H	2.39083000	5.82406700	-1.13360200
C	0.77249300	4.40110800	-0.95770800
C	-0.17091900	5.37308000	-0.53560300
H	0.16572400	6.39758500	-0.40899800
C	-1.47635900	5.03736800	-0.29442800
H	-2.19016700	5.78428200	0.03455100
C	-1.90966100	3.71967300	-0.54012100
H	-2.96187800	3.46811200	-0.44336400
C	-1.02197600	2.75391500	-0.94756600
C	0.36812900	3.03924200	-1.09874100
C	5.21960000	-1.66767600	0.50971900
H	4.91846300	-2.37744100	-0.26477500
C	6.70679800	-1.40201100	0.29358100
H	6.89187000	-0.99874800	-0.70546400
H	7.24720700	-2.34809200	0.38827000
H	7.11760600	-0.71199100	1.03699100
C	4.93225900	-2.26791700	1.88735000
H	3.85936300	-2.42995200	2.03780900
H	5.29079400	-1.61412000	2.68883800
H	5.44191100	-3.23071900	1.98899600
C	4.74412000	0.78249500	1.00685400
H	5.37372000	0.43298400	1.82973500
C	5.57342400	1.75880300	0.17641500
H	6.46780900	1.28077300	-0.22900000
H	5.88945700	2.59357100	0.80975200
H	4.99607500	2.16730400	-0.65322400
C	3.51971600	1.43112300	1.64431900
H	2.96556500	0.69922800	2.23871000
H	2.84583100	1.87208600	0.90446300
H	3.84712100	2.23511000	2.30919400
C	0.39176600	-2.97989500	-1.35718900
H	0.23826000	-4.05922400	-1.41608200
C	-0.64780400	-2.40955400	-0.39137100
H	-0.61405800	-2.92467900	0.57244000
H	-1.65322500	-2.52126800	-0.80738200
H	-0.47474100	-1.34416500	-0.20051000
C	0.28002600	-2.42522800	-2.77549900
H	1.04864700	-2.86360000	-3.41801900
H	0.39175700	-1.33627300	-2.81114700
H	-0.69969000	-2.67329300	-3.19251700
C	2.49613200	-3.98181500	-0.30885700
H	3.42979900	-3.58746000	0.09025500
C	1.75430200	-4.66169300	0.84021200
H	1.54240400	-3.94683400	1.64113500
H	2.37649800	-5.46319300	1.24828000
H	0.81121200	-5.10956400	0.50998700
C	2.83625300	-4.93717000	-1.45024500
H	3.37831700	-4.41378400	-2.24297400
H	1.93877000	-5.39094300	-1.88325800
H	3.46727500	-5.74685700	-1.07282600
C	-0.97612600	1.40629700	2.37791000
H	-0.62412600	1.74617700	1.40090000
C	0.16642000	0.64297500	3.04120000
H	0.51682900	-0.16966100	2.39578100
H	-0.12355300	0.22295600	4.00935900
H	0.99724700	1.33132500	3.21775600
C	-1.42098400	2.63483000	3.16615400
H	-2.22165000	3.15900100	2.63604000
H	-0.57700300	3.32094300	3.28109500
H	-1.77762100	2.37178300	4.16751500
C	-2.80354800	-0.18832400	3.20739300
H	-2.32305000	0.18720000	4.11345000
C	-2.54108900	-1.69249000	3.13946500
H	-1.46762900	-1.89224600	3.20668400
H	-2.90408400	-2.13393700	2.20606000
H	-3.04066700	-2.19941100	3.96969000
C	-4.27695100	0.20419100	3.28781300
H	-4.83001100	-0.06208700	2.38276700
H	-4.37365000	1.28370000	3.43445100
H	-4.75122000	-0.30452700	4.13141300
C	-5.02664100	-1.83339300	0.20481700
H	-4.59473100	-1.71547000	1.19887400
C	-6.48506300	-1.38466100	0.26442200
H	-6.55944300	-0.33846000	0.57675900
H	-7.02749700	-2.00115000	0.98672400
H	-6.98317500	-1.49258000	-0.70450600
C	-4.86591500	-3.29668900	-0.19978300
H	-3.81256100	-3.59258600	-0.18120700
H	-5.26797400	-3.49049000	-1.19935600
H	-5.41373500	-3.92907100	0.50443500
C	-4.54985100	-0.86794900	-2.11974800
H	-5.38912100	-1.55055600	-2.26653800
C	-3.38537000	-1.37301900	-2.96855800
H	-3.15914700	-2.41679000	-2.73198000
H	-2.47520700	-0.78265400	-2.81229200
H	-3.64211100	-1.30943900	-4.02946900
C	-5.01634100	0.53357100	-2.50771800
H	-5.85912400	0.84767700	-1.88569800
H	-5.33596200	0.53808200	-3.55326300
H	-4.21894600	1.27760300	-2.40339000

90•74^{-} (Catalyst-Enolate Complex)



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opt=calcfc freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

Zero-point correction= 1.353526 (Hartree/Particle)
Thermal correction to Energy= 1.426216
Thermal correction to Enthalpy= 1.427160
Thermal correction to Gibbs Free Energy= 1.245099
Sum of electronic and zero-point Energies= -2830.200290
Sum of electronic and thermal Energies= -2830.127599
Sum of electronic and thermal Enthalpies= -2830.126655
Sum of electronic and thermal Free Energies= -2830.308717

1 1

N	1.16499700	0.78084300	-1.64954000	C	3.64299200	-3.42570500	-2.82211000
H	0.17954500	1.02594500	-1.45856900	H	2.86430200	-3.52275200	-3.58315400
C	1.41365900	-0.44431100	-2.12514200	C	4.98425900	-3.57157800	-3.53588500
N	3.46837000	-2.07025800	-2.25757100	H	5.10096800	-2.80582400	-4.30766600
C	2.26871100	-1.51039100	-2.32715500	H	5.02872000	-4.55362000	-4.01515800
N	-0.08977400	-2.28728000	-3.19474200	H	5.82864900	-3.50491500	-2.84257700
C	0.92138600	-1.60868800	-2.68287900	C	3.42998100	-4.49525900	-1.74892700
N	0.88284200	1.59525400	1.02981000	H	2.46693300	-4.36029600	-1.24379300
H	-0.03520000	1.36524300	0.61437200	H	4.21841800	-4.46030300	-0.98973000
C	1.52942000	0.74620700	1.82138800	H	3.44602900	-5.49058800	-2.20264800
N	3.88805600	0.76330900	2.92350400	C	4.49512100	-1.53106400	-1.33858300
C	2.65589000	0.42035900	2.55027000	H	5.11392100	-2.39130600	-1.06943100
N	0.97132100	-1.61187300	2.74799800	C	5.38285200	-0.48987600	-2.01564500
C	1.58399900	-0.46559500	2.47996400	H	5.84296300	-0.88892400	-2.92315900
C	2.09586800	1.84673800	-1.73395400	H	6.18101200	-0.18451200	-1.33116500
C	2.85546800	1.95997200	-2.87641700	H	4.80355800	0.39969100	-2.27965600
H	2.74474100	1.21230900	-3.65657500	C	3.86662800	-0.99846400	-0.05677200
C	3.72999200	3.04578600	-3.07306100	H	3.15297100	-1.71634500	0.36147000
H	4.31925400	3.09838400	-3.98239600	H	3.35025600	-0.04899700	-0.22869100
C	3.78335200	4.04877800	-2.14457900	H	4.64604400	-0.81726000	0.68617500
H	4.41526900	4.91752200	-2.30212800	C	-1.31591000	-1.56550700	-3.60575800
C	3.00897500	3.97790500	-0.95757700	H	-1.87005100	-2.27544700	-4.22493100
C	3.07310200	5.03691100	-0.01256900	C	-2.16358400	-1.19389100	-2.39679600
H	3.69804800	5.89502700	-0.24176300	H	-2.44569500	-2.08617200	-1.83155600
C	2.36089200	4.98700200	1.15385300	H	-3.07664800	-0.67996800	-2.71062700
H	2.40186200	5.80374800	1.86636800	H	-1.62282400	-0.51830000	-1.72925500
C	1.59922400	3.83856000	1.45111600	C	-0.97625300	-0.35541900	-4.47380000
H	1.08242600	3.75367900	2.40143700	H	-0.32752900	-0.64043000	-5.30778600
C	1.53391700	2.78236000	0.57621700	H	-0.48140300	0.43203600	-3.89479100
C	2.18334100	2.83902100	-0.70127200	H	-1.89818400	0.07031500	-4.88007300

C	0.02215700	-3.74240900	-3.41179200	C	-1.36135000	-0.79128300	2.82003700
H	0.94986500	-4.03922300	-2.91850900	H	-1.29841800	-0.79690600	3.91242000
C	-1.11410600	-4.49258100	-2.71777700	H	-2.38657500	-1.03226900	2.53160900
H	-1.14861600	-4.24564400	-1.65210100	H	-1.14800300	0.22236700	2.46370800
H	-0.94986600	-5.56933500	-2.81935400	O	-1.19990700	1.56662400	-0.62314800
H	-2.08766800	-4.26317400	-3.16254700	C	-2.47008400	1.68613700	-0.61466800
C	0.13375000	-4.07285900	-4.89886900	C	-3.29968300	0.80753600	0.07126600
H	0.97200300	-3.53592600	-5.35398100	H	-2.79476100	-0.02328200	0.55787400
H	-0.77989600	-3.80436400	-5.43927000	N	-4.65124200	0.94779500	0.09521900
H	0.29603800	-5.14661500	-5.03098900	C	-5.45450700	0.11366900	0.67944100
C	4.44095000	2.04210800	2.42586400	C	-4.97988300	-1.13271900	1.36344900
H	3.78950500	2.34053900	1.60338600	C	-5.11775300	-1.30337900	2.74551200
C	5.84244300	1.85930300	1.84752400	C	-4.35866800	-2.14938400	0.62900600
H	5.84319100	1.10384000	1.05668600	C	-4.63996900	-2.45042700	3.37594100
H	6.57339900	1.56949400	2.60939600	H	-5.60480100	-0.52717100	3.32987100
H	6.17587900	2.80653500	1.41336200	C	-3.87219000	-3.29345600	1.25483900
C	4.38044400	3.12811400	3.49790000	H	-4.25351700	-2.02998100	-0.44531700
H	3.35839000	3.24520200	3.87110400	C	-4.00922200	-3.44676200	2.63386900
H	4.70294100	4.08389900	3.07420000	H	-4.75628300	-2.56385800	4.44981600
H	5.03545200	2.89633300	4.34495700	H	-3.39054100	-4.06834900	0.66413400
C	4.60093000	0.02990000	3.98715300	H	-3.63303600	-4.33947600	3.12490200
H	5.44443500	0.67106100	4.25477700	C	-6.90688400	0.40595200	0.65674600
C	5.18329300	-1.28531500	3.46814500	C	-7.85876200	-0.52815800	1.09265200
H	5.93224600	-1.08932600	2.69487200	C	-7.37537800	1.63906100	0.17062400
H	4.41731900	-1.93347700	3.03223000	C	-9.22106100	-0.24112700	1.04838700
H	5.66758700	-1.83144900	4.28312200	H	-7.53287000	-1.49429000	1.46613900
C	3.74392600	-0.10856900	5.24548400	C	-8.73324700	1.92241400	0.12406200
H	2.83370900	-0.68972800	5.07372000	H	-6.64634400	2.36562500	-0.17230600
H	3.44594900	0.87931500	5.60910900	C	-9.66877800	0.98461400	0.56493100
H	4.31558400	-0.60971700	6.03166300	H	-9.93551300	-0.98481000	1.39101000
C	1.64104000	-2.68713800	3.49621400	H	-9.06762700	2.88375600	-0.25730300
H	2.61563800	-2.28493100	3.77279000	H	-10.73116200	1.20768400	0.52947600
C	0.89250500	-3.01825400	4.78668500	O	-3.06725200	2.67533400	-1.31944200
H	0.74286200	-2.11635100	5.38786400	C	-2.32906400	3.77838800	-1.89534600
H	1.47396100	-3.73484800	5.37421300	C	-1.57233900	4.55069500	-0.81402300
H	-0.08629500	-3.46704000	4.58870600	H	-0.78808900	3.93574200	-0.37110400
C	1.87612200	-3.91353800	2.61445200	H	-1.11160200	5.44332000	-1.25073000
H	2.45671800	-3.64875800	1.72455700	H	-2.26246200	4.86985700	-0.02595700
H	0.93260400	-4.36477500	2.28979700	C	-1.39803700	3.30733600	-3.01621700
H	2.43142500	-4.67047900	3.17632300	H	-1.92958300	2.61559200	-3.67782700
C	-0.39721300	-1.81453800	2.22737500	H	-1.07195200	4.16840900	-3.60972700
H	-0.69991100	-2.80187300	2.58471000	H	-0.51308300	2.80846900	-2.62084100
C	-0.41898600	-1.84637600	0.70001500	C	-3.43901900	4.64998300	-2.48415000
H	0.29456500	-2.58212300	0.31201800	H	-3.99151800	4.09952600	-3.25235200
H	-0.18417900	-0.86689900	0.27136400	H	-4.14238700	4.95167300	-1.70210200
H	-1.42230400	-2.11477200	0.35856300	H	-3.01342300	5.55013000	-2.93867100

TS1$_u$ (Uncatalyzed Benzylation Transition State)

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opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

Zero-point correction= 0.471798 (Hartree/Particle)
Thermal correction to Energy= 0.500100
Thermal correction to Enthalpy= 0.501044
Thermal correction to Gibbs Free Energy= 0.410493
Sum of electronic and zero-point Energies= -3783.206422
Sum of electronic and thermal Energies= -3783.178120
Sum of electronic and thermal Enthalpies= -3783.177175
Sum of electronic and thermal Free Energies= -3783.267726

-1 1

O	2.42731500	0.77655000	2.43649100	C	3.78144900	-1.45865300	1.38935800
C	1.80738900	-0.05169100	1.76334800	C	0.03060100	0.28761900	-2.03712900
C	0.39182200	0.03596300	1.51213900	C	0.49544300	-0.55316400	-3.04062400
H	-0.12886800	0.75342900	2.14586700	C	1.86498800	-0.68282400	-3.26447400
N	-0.25475100	-0.95865700	0.85512600	C	2.76686700	0.04088200	-2.48405000
C	-1.53460000	-1.01700900	0.65559400	C	2.30204200	0.87498500	-1.47571400
C	-2.49975900	-0.01854700	1.21519800	C	0.92946500	0.99467300	-1.23048400
C	-3.24732400	0.81056500	0.37030200	H	-1.03571900	0.39168700	-1.86384100
C	-2.65214800	0.13184900	2.59834500	H	-0.21183700	-1.11379700	-3.64443100
C	-4.11469100	1.76761300	0.88980700	H	2.22896800	-1.34089100	-4.04814100
H	-3.14957300	0.69829900	-0.70650600	H	3.83486400	-0.05088900	-2.66102700
C	-3.52040100	1.08567100	3.12162700	H	3.00005800	1.43231000	-0.85755400
H	-2.07917000	-0.50621200	3.26571400	C	0.44208300	1.82735700	-0.13529200
C	-4.25360600	1.90812200	2.26881200	H	1.13439800	2.25618200	0.57335600
H	-4.68183500	2.40438400	0.21717300	H	-0.60648800	1.81219700	0.11626600
H	-3.62607700	1.18718000	4.19796400	Br	0.13301200	3.95481400	-1.20418900
H	-4.93018600	2.65368400	2.67605100	C	4.74420200	-0.37861200	0.89301800
C	-2.05211800	-2.11172100	-0.19854400	H	4.58614300	0.55729200	1.42975300
C	-3.42330200	-2.38748900	-0.30181900	H	5.77720700	-0.71034400	1.04662000
C	-1.16373400	-2.91118400	-0.93938200	H	4.59720000	-0.20594000	-0.17710200
C	-3.89066500	-3.41419100	-1.11954300	C	3.95038700	-2.72789400	0.55444800
H	-4.13417400	-1.79366500	0.26498400	H	4.97261100	-3.11050800	0.64265600
C	-1.63085900	-3.93458600	-1.75162500	H	3.25504500	-3.50351200	0.89098700
H	-0.10237700	-2.69890200	-0.86718300	H	3.74430000	-2.51332800	-0.49912400
C	-2.99986100	-4.19310500	-1.85139800	C	3.99743600	-1.76484300	2.87292300
H	-4.95892500	-3.60386200	-1.18239300	H	3.26371100	-2.50285400	3.21465700
H	-0.92361800	-4.53324100	-2.31995400	H	4.99935300	-2.18113100	3.02378800
H	-3.36377600	-4.99009200	-2.49354500	H	3.89434400	-0.85985400	3.47370000
O	2.40339000	-1.10083300	1.14512900				

TS1$_u$ (Uncatalyzed Benzylation Transition State - IRC precomplex)

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opt=calcfc freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

Zero-point correction= 0.471712 (Hartree/Particle)
Thermal correction to Energy= 0.500773
Thermal correction to Enthalpy= 0.501717
Thermal correction to Gibbs Free Energy= 0.407639
Sum of electronic and zero-point Energies= -3783.224171
Sum of electronic and thermal Energies= -3783.195110
Sum of electronic and thermal Enthalpies= -3783.194166
Sum of electronic and thermal Free Energies= -3783.288244

-1 1

O	-2.09305500	-0.04994300	-3.16590900	C	4.07722400	-0.45971400	-2.99561800
C	-1.61404900	-0.69374100	-2.22324400	H	2.70085300	-2.09180800	-2.72051100
C	-0.21920500	-0.76533900	-1.92810500	C	4.56666900	0.74006700	-2.48156400
H	0.43413700	-0.21301600	-2.60765200	H	4.41857600	2.17451700	-0.87920800
N	0.22865700	-1.39155000	-0.83574800	H	4.47037000	-0.85133700	-3.93004000
C	1.46244600	-1.40053600	-0.39723500	H	5.33862100	1.28825400	-3.01442600
C	2.56508800	-0.68041200	-1.10578400	C	1.73385700	-2.07903100	0.87776400
C	3.06570800	0.52683300	-0.60412300	C	3.03041600	-2.17762500	1.41569100
C	3.08592700	-1.16035600	-2.31324600	C	0.68411800	-2.65988800	1.62169700
C	4.05398600	1.23418100	-1.28405800	C	3.26275300	-2.80941300	2.63466900
H	2.65841200	0.92489500	0.32187000	H	3.86796600	-1.74965800	0.87205100

C	0.92035400	-3.28894500	2.83513800	H	-2.43955600	3.55514200	0.88158700
H	-0.32194600	-2.59675400	1.21830600	C	-0.30214100	2.22107200	-0.13720900
C	2.21319700	-3.37020000	3.35805200	H	-0.78658200	2.82868600	-0.89990300
H	4.27782500	-2.86454500	3.02089400	H	0.23331800	1.39411500	-0.60251400
H	0.08591400	-3.72290900	3.38133600	Br	1.10216400	3.40665300	0.61554700
H	2.39584600	-3.86112500	4.30963500	C	-4.20262800	0.20776900	-1.05334000
O	-2.39380700	-1.41385100	-1.35890000	H	-3.91741600	0.83683900	-1.89762200
C	-3.82334800	-1.25203900	-1.31149900	H	-5.28443100	0.28864000	-0.89711700
C	-1.08031300	0.50730100	1.51042800	H	-3.69583700	0.57074500	-0.15332900
C	-1.97400800	0.06156000	2.47970600	C	-4.22722200	-2.10474300	-0.10729700
C	-3.03703800	0.86963300	2.87678700	H	-5.31272400	-2.07319700	0.03590900
C	-3.20240000	2.12992200	2.30253000	H	-3.92570200	-3.14669600	-0.25647100
C	-2.30960800	2.57456400	1.33305300	H	-3.74336800	-1.72809500	0.80006300
C	-1.24642300	1.76345900	0.92617700	C	-4.47547200	-1.79566500	-2.58504500
H	-0.26816300	-0.13209800	1.18164000	H	-4.16308800	-2.83244100	-2.75214000
H	-1.83572400	-0.92129700	2.92150400	H	-5.56693500	-1.77802500	-2.48511100
H	-3.73699500	0.51985900	3.63008200	H	-4.18222700	-1.19638400	-3.44774000
H	-4.02990500	2.76376700	2.60750900				

TS1$_u$ (Uncatalyzed Benzylation Transition State - IRC product)

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opt=calcfc freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

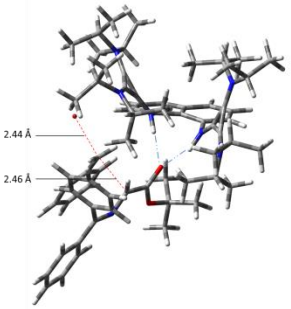
Zero-point correction= 0.475926 (Hartree/Particle)
Thermal correction to Energy= 0.503449
Thermal correction to Enthalpy= 0.504393
Thermal correction to Gibbs Free Energy= 0.415128
Sum of electronic and zero-point Energies= -3783.296141
Sum of electronic and thermal Energies= -3783.268618
Sum of electronic and thermal Enthalpies= -3783.267674
Sum of electronic and thermal Free Energies= -3783.356939

-1 1

O	2.97421600	1.00903300	-1.74094700	C	-3.27062800	-0.47787300	3.81613100
C	2.14922800	0.86831500	-0.85998400	H	-4.17101200	1.47212600	3.66096300
C	0.80464500	0.19018800	-1.11216500	H	-2.21139100	-2.35070400	3.70317900
H	0.28501800	0.86473400	-1.80898500	H	-3.84741100	-0.76501600	4.69072100
N	0.06400300	-0.04719100	0.10364600	O	2.26976600	1.30204300	0.38891900
C	-0.98401200	0.63010400	0.36065400	C	3.47569200	1.97986700	0.86318800
C	-1.45519800	1.80252500	-0.44771400	C	0.91508500	-3.14986800	-0.30995000
C	-2.52531600	1.67087100	-1.33537500	C	1.52800100	-4.09708900	0.50569000
C	-0.81205500	3.03519400	-0.31180400	C	2.91544400	-4.11576700	0.64168800
C	-2.94452700	2.76972000	-2.08075200	C	3.68548100	-3.18590800	-0.05248100
H	-2.99411000	0.69579600	-1.45197400	C	3.07040300	-2.24100500	-0.87150600
C	-1.24158800	4.13386000	-1.05133600	C	1.67911100	-2.20628800	-1.00409000
H	0.02566900	3.12693700	0.37460700	H	-0.16746400	-3.13111600	-0.42030500
C	-2.30918000	4.00207000	-1.93682100	H	0.91967700	-4.82275600	1.03876100
H	-3.76922200	2.66229700	-2.77935100	H	3.39309700	-4.85358600	1.28029400
H	-0.74118600	5.09108600	-0.93796000	H	4.76825200	-3.19708000	0.03997100
H	-2.64291100	4.85745800	-2.51699800	H	3.67586200	-1.51942300	-1.41379500
C	-1.78667900	0.25559500	1.55854400	C	1.00144600	-1.15398900	-1.84886900
C	-2.71760200	1.13797100	2.11296500	H	1.57683200	-0.95388400	-2.75827100
C	-1.61428400	-1.00542700	2.14148100	H	0.00248200	-1.49722500	-2.13609500
C	-3.45322500	0.77486200	3.23882700	Br	-2.84660200	-2.15846200	-1.50238900
H	-2.86785200	2.11586100	1.66592900	C	4.67862900	1.04682300	0.73759400
C	-2.34922100	-1.36771600	3.26219800	H	4.93800000	0.87420800	-0.30777300
H	-0.90140900	-1.69011500	1.69482700	H	5.53854300	1.49606600	1.24473900

H	4.46019700	0.08443200	1.21143200	C	3.67020400	3.29240500	0.10725400
C	3.15293900	2.24671400	2.33041800	H	2.76436300	3.90435000	0.17274700
H	3.99129500	2.76231100	2.80860600	H	4.49533700	3.85116200	0.56046500
H	2.26032100	2.87378100	2.41984600	H	3.90127800	3.11270400	-0.94361200
H	2.97218100	1.30656300	2.85967400				

TS1 (Catalyzed benzylation)



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opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

Zero-point correction= 1.474045 (Hartree/Particle)
Thermal correction to Energy= 1.555729
Thermal correction to Enthalpy= 1.556673
Thermal correction to Gibbs Free Energy= 1.354817
Sum of electronic and zero-point Energies= -5672.698146
Sum of electronic and thermal Energies= -5672.616462
Sum of electronic and thermal Enthalpies= -5672.615518
Sum of electronic and thermal Free Energies= -5672.817374

1 1

N	-2.09483400	-1.30141500	1.83910800	C	-0.43634700	2.68847100	2.07502400
H	-1.08983300	-1.49831700	1.78672800	H	0.20811000	3.07298800	1.28694600
C	-2.91382400	-1.97845400	1.03575100	C	-1.12085400	1.51924700	1.85108300
N	-5.31342600	-1.70121600	0.01915400	C	-1.91974300	0.93013500	2.88419000
C	-4.09850000	-2.12415800	0.34058100	C	-6.16932800	-2.56916700	-0.81641100
N	-2.53593100	-4.11345100	-0.40369800	H	-5.74905500	-3.57294800	-0.71237600
C	-3.06272700	-3.04488500	0.17340200	C	-7.59876600	-2.63142300	-0.28262800
N	-1.06552900	0.93429900	0.55118600	H	-7.60979000	-2.94537700	0.76474000
H	-0.54515100	0.06011400	0.47895800	H	-8.16666900	-3.36015500	-0.86800400
C	-1.31809500	1.63630000	-0.55967300	H	-8.11377400	-1.66925500	-0.36658700
N	-2.24040400	4.01780200	-1.07576400	C	-6.10486300	-2.15496400	-2.28599900
C	-1.76682800	2.78465600	-1.18120200	H	-5.07048400	-2.15252400	-2.64535800
N	-1.14238900	1.06895400	-3.09317900	H	-6.52070700	-1.15281600	-2.43597600
C	-1.34472700	1.69259400	-1.93326600	H	-6.68307700	-2.85251800	-2.89918300
C	-2.49827100	-0.37597700	2.83870000	C	-5.72193600	-0.30299800	0.28469200
C	-3.33815900	-0.81091200	3.83612400	H	-6.56045800	-0.12534800	-0.39323100
H	-3.73629900	-1.81986400	3.78388800	C	-6.21666700	-0.12190300	1.71733900
C	-3.63769500	0.01072600	4.94073500	H	-7.02345000	-0.82385800	1.94479500
H	-4.31445400	-0.34910800	5.70821700	H	-6.59463700	0.89596900	1.85478500
C	-3.01426800	1.22307800	5.07049700	H	-5.40563600	-0.28010400	2.43368200
H	-3.17991600	1.83704300	5.95070300	C	-4.62295500	0.69166800	-0.08665200
C	-2.12927200	1.69835500	4.06847500	H	-4.28096800	0.53151200	-1.11422500
C	-1.44686000	2.93259500	4.24250700	H	-3.76303100	0.61980700	0.58628400
H	-1.60891700	3.48919700	5.16071100	H	-5.01524700	1.71000800	-0.00865900
C	-0.58543700	3.39653600	3.28698100	C	-1.26264200	-4.66295900	0.11826400
H	-0.03736300	4.32118400	3.43328700	H	-1.18333200	-5.66212400	-0.31609300

C	-0.07333500	-3.83077000	-0.35773200
H	-0.02773600	-3.80916800	-1.45074900
H	0.86092300	-4.26153000	0.01590100
H	-0.12649700	-2.80108400	0.01196900
C	-1.30105500	-4.82695400	1.63651700
H	-2.17532400	-5.40900000	1.94352600
H	-1.32702600	-3.86193700	2.15172000
H	-0.40009300	-5.35005000	1.96887300
C	-3.30776000	-4.84688700	-1.42746500
H	-4.04922300	-4.13270900	-1.79483200
C	-2.44326400	-5.24483500	-2.62251900
H	-1.92748900	-4.37928400	-3.04737300
H	-3.08753200	-5.67110800	-3.39665700
H	-1.69772500	-6.00192600	-2.36218400
C	-4.02828000	-6.04248800	-0.80590400
H	-4.66871800	-5.72477000	0.02341400
H	-3.31041900	-6.77605200	-0.42325500
H	-4.65183300	-6.53976300	-1.55486700
C	-2.42705400	4.60715000	0.26453200
H	-2.29484400	3.77985500	0.96239200
C	-3.84895000	5.13297100	0.45220900
H	-4.58366500	4.36184200	0.20230800
H	-4.05194200	6.01885700	-0.15809500
H	-3.98953800	5.41709900	1.49943800
C	-1.35918200	5.65981600	0.55558000
H	-0.36202800	5.25868100	0.34735600
H	-1.41059300	5.95923900	1.60717700
H	-1.50676400	6.55723100	-0.05557700
C	-2.42025600	4.85855700	-2.27460500
H	-2.86958900	5.78360400	-1.90645300
C	-3.43409800	4.22785100	-3.22992400
H	-4.40624000	4.13749900	-2.73589200
H	-3.13605700	3.22823200	-3.55825100
H	-3.55247000	4.85232700	-4.11991300
C	-1.07442600	5.23101500	-2.90317900
H	-0.44333600	4.35712700	-3.08202000
H	-0.51118600	5.88643800	-2.23357100
H	-1.23066000	5.75320900	-3.85189600
C	-0.88765800	1.82855200	-4.33131200
H	-1.17710200	2.85408200	-4.10703900
C	0.60399800	1.83188600	-4.66966800
H	1.17870500	2.20235800	-3.81420900
H	0.78828300	2.48309200	-5.52977500
H	0.96121500	0.82768700	-4.92523400
C	-1.76473500	1.34374400	-5.48323200
H	-2.81996700	1.33187800	-5.19279500
H	-1.48728900	0.33991600	-5.82093000
H	-1.64724900	2.02020200	-6.33501400
C	-0.85363200	-0.37590500	-3.06251800
H	-0.71293000	-0.66612400	-4.10581300
C	-2.05515200	-1.13838600	-2.51070700
H	-2.95882900	-0.91490900	-3.08584600
H	-2.23582700	-0.86971700	-1.46388100
H	-1.86910100	-2.21530500	-2.54623100
C	0.42469700	-0.69906900	-2.30376100
H	1.27022500	-0.11490500	-2.67380100
H	0.67108500	-1.75712700	-2.41718000
H	0.30988100	-0.50395600	-1.23548700
O	0.59382900	-1.08769000	1.51980600
C	1.84501000	-1.22429500	1.56259100
C	2.64064500	-1.22299200	0.38965100
H	2.09153500	-1.38838000	-0.53160100
N	3.99423400	-1.40293000	0.45141200
C	4.72067300	-1.54947400	-0.60663500
C	4.13721600	-1.65659800	-1.98574300
C	4.22940100	-0.60183300	-2.89914600
C	3.46594800	-2.82176400	-2.37233900
C	3.65667000	-0.70475500	-4.16542400
H	4.76201300	0.30412300	-2.62200600
C	2.90124500	-2.93118600	-3.63980500
H	3.38721400	-3.64514500	-1.66747500
C	2.99160800	-1.87019200	-4.53901800
H	3.73359000	0.12542700	-4.86139800
H	2.38827000	-3.84531600	-3.92474700
H	2.54884200	-1.95307300	-5.52716400
C	6.19228000	-1.62577900	-0.44926600
C	7.02874600	-1.95982900	-1.52201500
C	6.78105400	-1.35959200	0.79746700
C	8.41012900	-2.02817500	-1.35485100
H	6.59787300	-2.17124700	-2.49606100
C	8.15699700	-1.42893800	0.96214700
H	6.13329400	-1.09031600	1.62477700
C	8.98149200	-1.76408500	-0.11401200
H	9.04007100	-2.29197800	-2.19979700
H	8.59350900	-1.21764700	1.93444500
H	10.05834000	-1.81746200	1.01669400
O	2.51521300	-1.32356400	2.71710300
C	1.87274200	-1.42847100	4.01630500
C	4.81040200	1.67973900	0.43875800
C	5.81411900	2.00749300	1.34136300
C	5.49581900	2.27417400	2.67179700
C	4.16736500	2.21894800	3.09666500
C	3.16552300	1.88801300	2.19591500
C	3.47774400	1.60480400	0.86050600
H	5.05658300	1.47240400	-0.59769200
H	6.84659600	2.04704400	1.00876400
H	6.28055800	2.52869200	3.37775500
H	3.91813000	2.43021000	4.13248900
H	2.13035000	1.83469200	2.51959800
C	2.43537800	1.18575400	-0.05957100
H	1.43317600	1.01938000	0.29687700
H	2.69585800	0.83316800	-1.04489100
Br	1.66243400	3.27541800	-1.06296200
C	1.19474100	-0.11493600	4.39902500
H	0.45915400	0.17465500	3.64893600
H	0.68385200	-0.23248800	5.36051900
H	1.93517000	0.68351100	4.50058700
C	0.89330600	-2.60390600	4.05666300
H	0.67435200	-2.85277700	5.10006100
H	-0.04815600	-2.36734200	3.55963200
H	1.33503000	-3.48430600	3.57904000
C	3.05556500	-1.70177900	4.94357500
H	3.52614600	-2.65889700	4.69867900
H	3.80383500	-0.90994500	4.84061000
H	2.71838700	-1.73335700	5.98437100

TS1 (Catalyzed benzylation – IRC precomplex)

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opt=calcfc freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

Zero-point correction= 1.475825 (Hartree/Particle)
Thermal correction to Energy= 1.557387
Thermal correction to Enthalpy= 1.558331
Thermal correction to Gibbs Free Energy= 1.356719
Sum of electronic and zero-point Energies= -5672.715369
Sum of electronic and thermal Energies= -5672.633807
Sum of electronic and thermal Enthalpies= -5672.632863
Sum of electronic and thermal Free Energies= -5672.834475

1 1

N	-2.22911400	-1.55766200	1.43945200	C	-4.36795300	1.14374300	0.02028600
H	-1.26805200	-1.89526100	1.28415000	H	-4.06852700	1.06232200	-1.02957600
C	-3.17067100	-1.91610200	0.56848500	H	-3.53616400	0.81506300	0.65213400
N	-5.51948000	-1.05138900	-0.21077000	H	-4.55062700	2.19937500	0.23956400
C	-4.38283600	-1.72236600	-0.06407200	C	-2.01319000	-4.55566200	-1.01798900
N	-3.20161700	-3.71976100	-1.31039000	H	-2.12014500	-5.43382600	-1.65906200
C	-3.52079400	-2.73452800	-0.48789600	C	-0.72491400	-3.82879000	-1.39873600
N	-0.69819900	0.65235600	0.76619500	H	-0.73190400	-3.55807200	-2.45904500
H	-0.26231400	-0.24165700	0.49136700	H	0.13718300	-4.47823400	-1.21715500
C	-1.01307000	1.59202800	-0.12262800	H	-0.57732900	-2.92407000	-0.79963200
N	-1.92222400	4.02381500	0.08865100	C	-2.01313200	-5.04301900	0.42946000
C	-1.48096600	2.86654600	-0.38700300	H	-2.96136700	-5.53058600	0.67579600
N	-1.05289700	1.71521500	-2.72742600	H	-1.84452800	-4.22533800	1.13657400
C	-1.14345300	2.00951600	-1.42919900	H	-1.20465800	-5.76633100	0.56873900
C	-2.47107000	-0.86827300	2.65569000	C	-4.12496900	-4.09108900	-2.40118800
C	-3.41264300	-1.36947800	3.52410200	H	-4.78478000	-3.22976200	-2.52662100
H	-3.99192300	-2.23870500	3.22657400	C	-3.39478200	-4.28986600	-3.72761600
C	-3.59489700	-0.80677800	4.80317000	H	-2.81752900	-3.40142600	-3.99795100
H	-4.35260500	-1.21429300	5.46385000	H	-4.13321900	-4.46934200	-4.51433100
C	-2.77068600	0.20168100	5.22489100	H	-2.72036000	-5.15131600	-3.70613500
H	-2.86002600	0.60532800	6.22894200	C	-4.96649800	-5.30442200	-2.00790100
C	-1.77870200	0.73667800	4.36329100	H	-5.50297400	-5.11788700	-1.07190500
C	-0.90469200	1.75590400	4.82881300	H	-4.34032800	-6.19296000	-1.87350100
H	-1.00254200	2.09187600	5.85684700	H	-5.69901500	-5.52423900	-2.79013100
C	0.04777300	2.29351600	4.00760300	C	-2.01305200	4.21654300	1.55145900
H	0.73049500	3.05514400	4.36835800	H	-1.84599900	3.22921600	1.98210300
C	0.11636000	1.88212300	2.66083200	C	-3.40989200	4.66288600	1.98030000
H	0.81811300	2.35540500	1.98114000	H	-4.17403400	3.97553800	1.60607500
C	-0.73169900	0.92157700	2.16731400	H	-3.65073200	5.67479900	1.63975600
C	-1.66101200	0.25165400	3.02554400	H	-3.46012400	4.66496900	3.07330800
C	-6.52724600	-1.56761900	-1.16034700	C	-0.91688500	5.15419500	2.05252000
H	-6.31963300	-2.63756400	-1.24956100	H	0.06366800	4.81581800	1.70352800
C	-7.94129700	-1.43863100	-0.59835100	H	-0.91261100	5.17108800	3.14660100
H	-8.01757200	-1.92712500	0.37691900	H	-1.07673500	6.17925500	1.69999700
H	-8.64320800	-1.92272700	-1.28340300	C	-2.19721400	5.15422200	-0.81767500
H	-8.25195000	-0.39441700	-0.49284800	H	-2.61641700	5.93482200	-0.17914600
C	-6.37570100	-0.91443700	-2.53445500	C	-3.27751400	4.78297600	-1.83376300
H	-5.36238600	-1.05455800	-2.92637700	H	-4.21452900	4.55524600	-1.31678900
H	-6.57572200	0.16126500	-2.48607800	H	-3.00737900	3.90677200	-2.43009400
H	-7.08330600	-1.35593700	-3.24251100	H	-3.45374700	5.61581200	-2.52039500
C	-5.63595000	0.33660300	0.29320900	C	-0.90673600	5.71746100	-1.41854900
H	-6.43765100	0.78302400	-0.30005900	H	-0.32832500	4.95710600	-1.94962200
C	-6.04806700	0.37616400	1.76173900	H	-0.26442700	6.11924600	-0.62951100
H	-6.98325800	-0.16753200	1.92100000	H	-1.13788000	6.52431000	-2.12003300
H	-6.19294200	1.41410400	2.07837900	C	-0.83561500	2.77539400	-3.72853800
H	-5.27457700	-0.06572300	2.39578500	H	-1.08803300	3.70714000	-3.22371200

C	0.63956200	2.84458500	-4.12782200	C	8.46594100	-1.78075700	-1.29701400
H	1.25851500	3.00045700	-3.23830600	H	6.80955300	-1.61413000	-2.64862100
H	0.80289300	3.67638700	-4.82008100	C	7.91554700	-1.97758800	1.03437700
H	0.96696500	1.92367800	-4.62318200	H	5.81321400	-1.94235000	1.50535200
C	-1.77779100	2.63507200	-4.92166800	C	8.87836100	-1.91331000	0.02582800
H	-2.81654300	2.54557400	-4.58888900	H	9.20266300	-1.73423800	-2.09449300
H	-1.53564600	1.76647600	-5.54220700	H	8.22235700	-2.07637600	2.07248400
H	-1.69199100	3.52309600	-5.55463500	H	9.93566800	-1.96535400	0.26929500
C	-0.86788700	0.30403000	-3.11299000	O	2.19171700	-2.80584900	2.02279900
H	-0.77585400	0.31022400	-4.20089100	C	1.57269200	-2.93527800	3.32059300
C	-2.10809400	-0.50262900	-2.73770000	C	4.97220400	2.04780200	0.45812400
H	-3.00758500	-0.07573900	-3.19190700	C	6.01365800	1.91473900	1.36837200
H	-2.23926300	-0.51508900	-1.64984700	C	5.80827500	1.23301000	2.56723200
H	-2.00085100	-1.53892200	-3.06820000	C	4.55961200	0.68659300	2.84934000
C	0.40005200	-0.30456600	-2.53179700	C	3.51933300	0.81409600	1.93386200
H	1.28388800	0.29670900	-2.76252900	C	3.72029200	1.48982800	0.73079100
H	0.55886900	-1.30469100	-2.94349700	H	5.12469300	2.59051700	-0.47180500
H	0.32261600	-0.41644200	-1.44843200	H	6.98625900	2.34166400	1.14445500
O	0.41372600	-1.79722900	0.99204200	H	6.62215100	1.12581000	3.27782500
C	1.64548200	-2.12870800	0.98432700	H	4.39772300	0.15306500	3.78134000
C	2.50079200	-1.85231600	-0.07775800	H	2.55167200	0.36743400	2.14155600
H	2.04580000	-1.42278500	-0.96459900	C	2.61326400	1.58800800	-0.26411800
N	3.84773200	-2.00917500	0.02584500	H	1.76847500	0.95499800	-0.00164100
C	4.68494500	-1.69384000	-0.91118500	H	2.93468600	1.37128400	-1.28143300
C	4.26175700	-1.21233000	-2.26550600	Br	1.88891100	3.43582200	-0.37189700
C	4.58569300	0.07650900	-2.70600600	C	1.36163000	-1.56346000	3.95837300
C	3.51591200	-2.03491600	-3.11706300	H	0.71042300	-0.94645200	3.33890200
C	4.15343900	0.54176600	-3.94585400	H	0.89687900	-1.67434600	4.94388100
H	5.18573800	0.71602300	-2.06367500	H	2.32051200	-1.05143000	4.08719700
C	3.09711000	-1.58132300	-4.36486100	C	0.26920600	-3.73703000	3.25770900
H	3.25921400	-3.03882100	-2.78979200	H	0.02381800	-4.11648900	4.25539900
C	3.40598900	-0.28759100	-4.78014400	H	-0.56760000	-3.12964000	2.91231200
H	4.40471000	1.55021800	-4.26231200	H	0.38628000	-4.59123500	2.58357900
H	2.52084900	-2.23702100	-5.01160000	C	2.62073200	-3.72457000	4.10625400
H	3.07226600	0.07119900	-5.74960100	H	2.76735300	-4.71374500	3.66089500
C	6.13251200	-1.77282900	-0.60590000	H	3.57813900	-3.19493900	4.09460000
C	7.11020800	-1.71211600	-1.60951300	H	2.30163800	-3.85272500	5.14540700
C	6.56467900	-1.90622300	0.72427500				

TS1 (Catalyzed benzylation – IRC product)

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opt=calcfc freq=noraman wb97xd/6-31g(d)/def2sv scrf=(iefpcm,solvent=dichloromethane)

Zero-point correction= 1.480009 (Hartree/Particle)
Thermal correction to Energy= 1.561225
Thermal correction to Enthalpy= 1.562169
Thermal correction to Gibbs Free Energy= 1.360549
Sum of electronic and zero-point Energies= -5672.775055
Sum of electronic and thermal Energies= -5672.693839
Sum of electronic and thermal Enthalpies= -5672.692895
Sum of electronic and thermal Free Energies= -5672.894514

1 1

N	-1.19889700	1.03192800	-2.16053000	C	-2.80721100	2.95424500	-1.34008600
H	-0.22650600	0.84543400	-1.92323500	N	-0.62628600	4.35557200	-0.85395700
C	-1.73514800	2.17360500	-1.72834200	C	-1.50171400	3.43176400	-1.21488500
N	-4.10787100	3.14257400	-1.17734900	N	-1.22908900	-0.98260600	-0.27086900

H	-0.31904500	-0.53794500	-0.19164400
C	-1.97574000	-1.09131800	0.82953300
N	-4.13773100	-2.38754200	1.46068100
C	-3.07023500	-1.59560800	1.49121300
N	-1.84123300	0.05603900	3.15066000
C	-2.21856300	-0.69895800	2.12271800
C	-1.83437800	0.08132900	-3.00386200
C	-2.34291400	0.50770200	-4.20781900
H	-2.31453700	1.56733100	-4.44530600
C	-2.84408300	-0.41523800	-5.14792700
H	-3.25298500	-0.05429800	-6.08554900
C	-2.74557700	-1.75805400	-4.89825000
H	-3.06909400	-2.48228200	-5.63990100
C	-2.21660100	-2.23461500	-3.67054900
C	-2.08930800	-3.62990700	-3.43505200
H	-2.38130900	-4.31712100	-4.22375100
C	-1.60234400	-4.10016900	-2.24563100
H	-1.48650700	-5.16539800	-2.07558300
C	-1.28694600	-3.19498800	-1.21058200
H	-0.97841100	-3.54589500	-0.22745100
C	-1.42242400	-1.84212300	-1.39572300
C	-1.81633000	-1.30652500	-2.66245700
C	-4.58308300	4.48201100	-0.77119100
H	-3.77791400	5.16899200	-1.04561200
C	-5.81537300	4.90276300	-1.56887900
H	-5.62482500	4.83302400	-2.64337200
H	-6.05868400	5.94164600	-1.32841500
H	-6.69258000	4.29453600	-1.32695400
C	-4.80207900	4.55189300	0.73979300
H	-3.89217100	4.26762900	1.27943000
H	-5.60906700	3.88228900	1.05565000
H	-5.07480100	5.56991200	1.03333800
C	-5.03340500	1.98741300	-1.12787100
H	-5.92495000	2.36630800	-0.62240300
C	-5.43245000	1.52212600	-2.52539300
H	-5.86067500	2.34368100	-3.10603800
H	-6.17834600	0.72458700	-2.45118400
H	-4.56769900	1.12559500	-3.06521000
C	-4.46698400	0.85532800	-0.27536000
H	-4.14371500	1.22431400	0.70382600
H	-3.61667700	0.36975100	-0.76513300
H	-5.23387000	0.09161600	-0.11771900
C	0.77400100	4.22860500	-1.31819900
H	1.22787900	5.20594200	-1.13866600
C	1.53039600	3.18791100	-0.49554000
H	1.59982400	3.49031800	0.55307100
H	2.54568700	3.06536700	-0.88612100
H	1.04219400	2.20904800	-0.53306000
C	0.84309400	3.96438100	-2.82156900
H	0.27549800	4.71919900	-3.37390700
H	0.45241600	2.97598700	-3.08346800
H	1.88515900	4.00424200	-3.15129800
C	-1.08331100	5.58054000	-0.16846100
H	-2.07759400	5.34188400	0.21744700
C	-0.20601100	5.91295400	1.03658100
H	-0.16201500	5.07165600	1.73372000
H	-0.63522200	6.77067700	1.56194100
H	0.81429700	6.18246100	0.74617600
C	-1.19907300	6.74259400	-1.15364600
H	-1.86767600	6.48424200	-1.98140900
H	-0.22164200	7.00509700	-1.57225100
H	-1.59800800	7.62717000	-0.64863100
C	-4.31920200	-3.26450800	0.28697400
H	-3.68503200	-2.83201000	-0.48872600
C	-5.75423700	-3.22643700	-0.23324700
H	-6.08269900	-2.19631300	-0.40124400
H	-6.46015700	-3.71145500	0.44853800
H	-5.80090800	-3.76197800	-1.18632500
C	-3.82692400	-4.68231800	0.57465500
H	-2.82603100	-4.65134400	1.01890000
H	-3.78890000	-5.25919400	-0.35516900
H	-4.50073200	-5.20152900	1.26586700
C	-4.92435300	-2.60970300	2.68658000
H	-5.73940500	-3.27255400	2.38770900
C	-5.56900900	-1.29948300	3.14355800
H	-6.25144300	-0.93126900	2.37135200
H	-4.83123600	-0.51464600	3.33436200
H	-6.13715800	-1.45777000	4.06471200
C	-4.10898700	-3.34270400	3.75931300
H	-3.10662000	-2.92178500	3.87650500
H	-3.96817900	-4.39019900	3.47989100
H	-4.62545600	-3.30926500	4.72347000
C	-2.31067700	-0.23458000	4.51673100
H	-3.11609900	-0.95817500	4.39695000
C	-1.21236200	-0.90330300	5.34338600
H	-0.82455500	-1.77580800	4.80685200
H	-1.61947700	-1.22479000	6.30734800
H	-0.38457300	-0.21327100	5.54293100
C	-2.89845800	1.00809700	5.18115400
H	-3.68333200	1.44793700	4.55760300
H	-2.13744100	1.77267700	5.36964600
H	-3.33521900	0.73428200	6.14623800
C	-0.71228700	0.98171300	2.94821200
H	-0.56895100	1.48086600	3.90959900
C	-1.07906600	2.04557000	1.91563000
H	-1.99946000	2.56831400	2.19490100
H	-1.22583800	1.59423600	0.92792400
H	-0.27044200	2.77603700	1.82918700
C	0.58650900	0.26534700	2.59085600
H	0.83655700	-0.50658500	3.32102500
H	1.40078900	0.99424600	2.54492600
H	0.51245400	-0.22674900	1.61838300
O	1.22684200	-0.12566600	-1.24319800
C	2.43429500	-0.34760400	-1.20768200
C	3.15442800	-0.47395200	0.12550400
H	2.63121000	0.20457000	0.80693600
N	4.55710600	-0.16106500	-0.00842900
C	5.13379000	0.58715800	0.85118200
C	4.44873400	1.20521500	2.03741900
C	4.26887600	0.48256000	3.21881700
C	3.98982300	2.52244400	1.96236900
C	3.63425800	1.07084500	4.31010100
H	4.63387500	-0.53805500	3.28873700
C	3.34035900	3.10392000	3.04788900
H	4.14401000	3.09153800	1.05041300
C	3.16442200	2.37940200	4.22525500
H	3.50139800	0.50275700	5.22535700
H	2.97972500	4.12590300	2.97547900
H	2.66573500	2.83432300	5.07551900
C	6.58281800	0.88266900	0.66176100
C	7.32349200	1.53721700	1.65063400
C	7.22278200	0.49625900	-0.52345900

C	8.67929700	1.79425000	1.46202800	H	1.60549200	-5.79650200	-1.53378000
H	6.84454300	1.84240200	2.57549600	H	1.32085400	-3.98392100	0.13263800
C	8.57296700	0.75636200	-0.71131900	C	2.95695500	-1.91959100	0.67245100
H	6.64177100	-0.00566200	-1.29016900	H	1.94285300	-2.01219800	1.07767200
C	9.30665200	1.40574600	0.28267700	H	3.63874400	-2.01170100	1.52556400
H	9.24382200	2.29831400	2.24049200	Br	-0.30870900	-3.48590500	2.39574500
H	9.05737100	0.45424800	-1.63496700	C	1.73422400	-1.93401500	-3.63663100
H	10.36341900	1.60688700	0.13501700	H	0.83789400	-1.75534700	-3.04125200
O	3.19502800	-0.53667000	-2.25096400	H	1.42763200	-2.12379400	-4.67014300
C	2.67587100	-0.73435700	-3.61758900	H	2.24168700	-2.82383000	-3.25337300
C	4.36956300	-3.12893800	-1.07529200	C	2.02005100	0.54724900	-4.12149400
C	4.54245400	-4.15736200	-1.99626500	H	1.87217200	0.46998800	-5.20284700
C	3.54637600	-5.11724800	-2.17544100	H	1.04522300	0.71359400	-3.66183900
C	2.38355200	-5.04773800	-1.41374300	H	2.66160600	1.41135200	-3.92271800
C	2.21133000	-4.01725000	-0.49109600	C	3.94996800	-1.03577000	-4.39876000
C	3.19407400	-3.03923800	-0.32054800	H	4.64221100	-0.18947900	-4.35333600
H	5.13813000	-2.37222200	-0.95331600	H	4.44337900	-1.91887900	-3.98329600
H	5.45937000	-4.20985300	-2.57701500	H	3.70420400	-1.22980100	-5.44679900
H	3.68124200	-5.91599400	-2.89917300				

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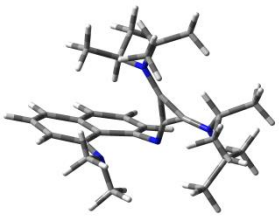

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

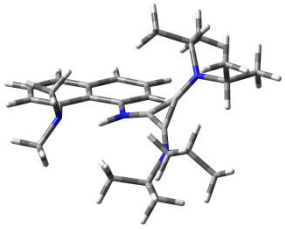
Zero-point correction= 0.624674 (Hartree/Particle)
Thermal correction to Energy= 0.658938
Thermal correction to Enthalpy= 0.659883
Thermal correction to Gibbs Free Energy= 0.558061
Sum of electronic and zero-point Energies= -1271.318395
Sum of electronic and thermal Energies= -1271.284130
Sum of electronic and thermal Enthalpies= -1271.283186
Sum of electronic and thermal Free Energies= -1271.385008

0 1

				C	-4.00514500	-0.45072300	-0.59944200
N	-0.37809600	-1.56534000	-0.82903900	C	-4.94204100	0.18991400	0.25886700
C	0.44922500	-0.62278500	-0.50974200	H	-5.90807100	0.47341900	-0.14993500
N	0.50782500	2.01851500	-0.17890300	C	-4.62606700	0.45045700	1.56615100
C	0.87392500	0.71369800	-0.27657100	H	-5.33623600	0.95102100	2.21878400
N	3.05047200	-0.81800400	-0.14691400	C	-3.39342600	0.01049900	2.09273800
C	1.79606800	-0.30962400	-0.24558500	C	-2.44935900	-0.64326700	1.31123500
C	-1.72942600	-1.28866800	-1.08387100	C	-2.69537500	-0.81571600	-0.10935500
C	-2.16160000	-1.54571100	-2.38491500	C	1.49446400	3.10813100	-0.06185000
H	-1.42412600	-1.93734100	-3.07823600	H	0.91600200	4.02931300	-0.17621000
C	-3.46731700	-1.26821200	-2.81708000	C	2.12293700	3.15256300	1.33946500
H	-3.74782700	-1.47187200	-3.84719200	H	1.34931400	3.30091600	2.09788300
C	-4.36837400	-0.69971100	-1.94729000	H	2.84313800	3.97400800	1.41585300
H	-5.36913800	-0.43066600	-2.27358500	H	2.64461900	2.22268900	1.58113100

C	2.52914600	3.09612700	-1.19764200	H	1.81179900	-2.41701000	-2.10047700
H	2.03254500	3.17690800	-2.16855500	H	3.14231300	-3.58286100	-2.18521400
H	3.12074800	2.17792600	-1.20466500	C	4.19193900	-0.00698500	0.30544400
H	3.21936700	3.93989100	-1.09439300	H	3.79231500	0.99822500	0.44976400
C	-0.90638100	2.35764600	-0.47263200	C	4.73700100	-0.48309100	1.66180700
H	-1.43417900	1.40354200	-0.46896900	H	3.94423300	-0.49352700	2.41532000
C	-1.52840100	3.22580000	0.62822200	H	5.53349200	0.18406300	2.00816900
H	-1.42151700	2.74831400	1.60562600	H	5.15797600	-1.49173200	1.59639200
H	-2.59722200	3.35428600	0.43293600	C	5.30076200	0.08896200	-0.75442700
H	-1.08021700	4.22479300	0.67623200	H	4.90390900	0.46021600	-1.70368200
C	-1.07647600	2.98196200	-1.86567100	H	5.77207200	-0.88130200	-0.94057700
H	-0.66719900	2.32420400	-2.63779000	H	6.08546800	0.77434300	-0.41750200
H	-0.58258600	3.95739000	-1.94183200	N	-1.26653200	-1.15424200	1.90771000
H	-2.13903200	3.13381600	-2.08026600	H	-3.21043300	0.14183200	3.15227400
C	3.24512100	-2.25136800	-0.47398500	C	-1.16691000	-2.61515300	1.90415400
H	4.31622200	-2.43144300	-0.34055300	H	-1.87137400	-3.07361200	2.62074400
C	2.48029400	-3.17633100	0.48259300	H	-1.36239300	-3.00730800	0.90837600
H	2.72962400	-2.95950200	1.52600300	H	-0.15066100	-2.90765100	2.18494200
H	2.74005600	-4.22095000	0.27951000	C	-0.87781000	-0.60153900	3.19357500
H	1.40207200	-3.06224700	0.34060500	H	-0.88583200	0.49079200	3.15309900
C	2.88607600	-2.54716600	-1.93759600	H	-1.51719300	-0.92210100	4.03704900
H	3.43229600	-1.88689600	-2.61821800	H	0.14288000	-0.92864900	3.41757700

102



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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

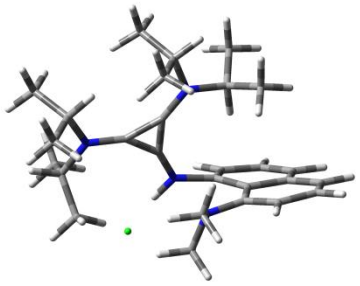
Zero-point correction= 0.638791 (Hartree/Particle)
Thermal correction to Energy= 0.672982
Thermal correction to Enthalpy= 0.673926
Thermal correction to Gibbs Free Energy= 0.572881
Sum of electronic and zero-point Energies= -1271.756541
Sum of electronic and thermal Energies= -1271.722349
Sum of electronic and thermal Enthalpies= -1271.721405
Sum of electronic and thermal Free Energies= -1271.822451

1 1

N	-0.80669400	-0.40476600	-0.35234700	H	-4.64157400	3.01007500	-1.69605900
H	-1.19707200	-1.29021000	0.04220000	C	-4.18883200	1.18231300	-0.63374000
C	0.49516700	-0.11008100	-0.22687800	C	-5.52510900	0.99561000	-0.19391100
N	2.07473100	1.94496300	0.33030000	H	-6.26926900	1.73593500	-0.47170500
C	1.56391400	0.74659900	0.04501200	C	-5.87546200	-0.09846800	0.55850800
N	2.59393900	-1.66605200	-0.35747200	H	-6.89901600	-0.23544100	0.89171400
C	1.78795200	-0.61867900	-0.21386000	C	-4.90023800	-1.06375900	0.88212100
C	-1.83510400	0.49321100	-0.71692600	C	-3.58623200	-0.92884200	0.47775400
C	-1.56276400	1.57181300	-1.53706200	C	-3.17760600	0.22308200	-0.27339700
H	-0.55823100	1.69843400	-1.92731400	C	3.55326100	2.12958400	0.22070600
C	-2.57486300	2.48768800	-1.89311100	H	3.89191500	1.30437000	-0.41164600
H	-2.33134000	3.32802300	-2.53518600	C	3.91694000	3.42727500	-0.50897100
C	-3.85641300	2.30734100	-1.43570000	H	3.44081400	3.47811900	-1.49143900

H	5.00036500	3.46439600	-0.65445200	H	2.01626900	-2.25830200	-2.95897800
H	3.63603400	4.31609300	0.06293300	H	0.44298100	-2.14933100	-2.14387300
C	4.24862900	2.02037300	1.58495400	H	1.06631900	-3.72047500	-2.65517600
H	3.98947800	1.08816800	2.09631300	C	4.04151500	-1.56930900	-0.01813600
H	3.98386100	2.85165000	2.24509600	H	4.15966000	-0.58331400	0.43525500
H	5.33424900	2.04661800	1.45186400	C	4.45006100	-2.60617600	1.03544700
C	1.27507300	3.00651700	1.02263400	H	3.83102000	-2.52488600	1.93313100
H	2.02453000	3.57620900	1.57914800	H	5.49132900	-2.43791500	1.32477600
C	0.57942000	3.96866300	0.05384900	H	4.38131400	-3.63023200	0.65661000
H	1.27208200	4.36905100	-0.68920900	C	4.91748400	-1.63233200	-1.27530500
H	0.16572900	4.81133100	0.61653200	H	4.63279000	-0.86092400	-1.99688700
H	-0.24634800	3.47928200	-0.46511900	H	4.84891300	-2.60523300	-1.77157200
C	0.30255300	2.41432400	2.04660900	H	5.96631300	-1.47860400	-1.00542900
H	0.81655400	1.75200000	2.74938500	N	-2.62622300	-1.98848900	0.78374500
H	-0.50941500	1.86092700	1.56698500	H	-5.19490700	-1.94065400	1.45001800
H	-0.15312900	3.22662700	2.61929000	C	-2.99366300	-3.27600900	0.16500100
C	2.04911500	-2.94900700	-0.89171400	H	-3.91063900	-3.70942100	0.58810300
H	2.92913100	-3.57424800	-1.05894300	H	-3.14175000	-3.13467800	-0.90782800
C	1.15739500	-3.65580700	0.13623300	H	-2.17869400	-3.99019200	0.31680800
H	1.68932100	-3.82682900	1.07523300	C	-2.38189300	-2.12709400	2.23076300
H	0.83575100	-4.62570100	-0.25455500	H	-2.06396300	-1.16528300	2.64043200
H	0.25749000	-3.07219900	0.35429500	H	-3.27146400	-2.46091300	2.78324500
C	1.35264300	-2.74916300	-2.24193400	H	-1.58532800	-2.85992200	2.39272900

95•HCl



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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

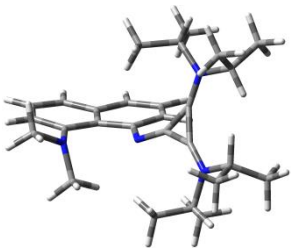
Zero-point correction= 0.640061 (Hartree/Particle)
Thermal correction to Energy= 0.676390
Thermal correction to Enthalpy= 0.677334
Thermal correction to Gibbs Free Energy= 0.571265
Sum of electronic and zero-point Energies= -1732.077913
Sum of electronic and thermal Energies= -1732.041584
Sum of electronic and thermal Enthalpies= -1732.040640
Sum of electronic and thermal Free Energies= -1732.146709

0 1

N	0.43057100	-1.37455000	-0.55817400	C	-0.46168000	-0.41406000	-0.40106700
H	0.11009500	-2.39585200	-0.70156300	C	-1.78704200	-0.04202800	-0.17114300
N	-3.05053500	-0.41478500	0.08205300	C	-0.81721500	0.93342300	-0.40235200
N	-0.38022200	2.20010800	-0.55803100	C	1.82012700	-1.14415500	-0.78918700
N	1.14872700	-0.65370300	2.11467800	C	2.69401900	-0.52094400	0.16916200
				C	2.35504000	-0.18120600	1.53787200

C	3.24133700	0.59069600	2.27775300	H	-4.50234800	-1.83095700	0.36976900
H	2.99668400	0.84753600	3.30200600	C	-2.70112900	-2.66893600	1.15075800
C	4.49424600	0.99290700	1.76749800	H	-3.18358100	-3.64604600	1.26035700
H	5.15556100	1.58973200	2.39027500	H	-1.66753900	-2.87309700	0.85899200
C	4.89496900	0.57436100	0.52479600	H	-2.72833500	-2.16050000	2.12162900
H	5.88129000	0.82227000	0.14125500	C	-3.34875200	-2.47921700	-1.31204200
C	4.02303900	-0.19881600	-0.28996800	H	-3.79886900	-3.47747200	-1.29780100
C	4.46833900	-0.64670800	-1.56129500	H	-3.88249200	-1.86990200	-2.05013600
H	5.48643400	-0.41244200	-1.86232200	H	-2.30970200	-2.62131300	-1.62359000
C	3.64139500	-1.37082400	-2.38641300	C	1.00584500	2.40251300	-1.06491500
H	3.99558200	-1.73725700	-3.34562300	H	1.46561600	1.41485900	-1.03936300
C	2.30487100	-1.59389700	-2.00610600	C	1.01664200	2.88494800	-2.52244100
H	1.62009800	-2.11920300	-2.66368800	H	2.04827600	2.92865100	-2.88821400
C	0.66423700	0.04682500	3.29388200	H	0.45785700	2.19898300	-3.16743900
H	-0.36288600	-0.27913200	3.49142400	H	0.58799500	3.88865500	-2.62793500
H	1.25376800	-0.15130100	4.20797100	C	1.82603000	3.31397400	-0.14422000
H	0.65625900	1.12656900	3.11614200	H	2.87001100	3.31747700	-0.47411200
C	1.09633600	-2.11118900	2.30909500	H	1.47282800	4.35200900	-0.15946800
H	0.07026100	-2.40559500	2.54764800	H	1.80448200	2.94742700	0.88573000
H	1.38987000	-2.64496700	1.40602100	C	-1.26478000	3.37963400	-0.43959300
H	1.75396000	-2.42705800	3.13730300	H	-0.61395200	4.23028700	-0.65767800
C	-4.09443700	0.59999300	0.34032700	C	-2.37743300	3.40281900	-1.49987000
H	-3.58776800	1.56154500	0.26296000	H	-2.98095600	4.31113700	-1.39231600
C	-4.65022400	0.49363500	1.76914400	H	-1.94798300	3.39680600	-2.50629700
H	-5.34990300	1.31551300	1.95881000	H	-3.04985200	2.54464300	-1.42406500
H	-5.19256900	-0.44396600	1.93002200	C	-1.76169500	3.57262900	1.00060000
H	-3.84342100	0.55081100	2.50720100	H	-2.38727700	4.46935900	1.07116500
C	-5.20724200	0.57955300	-0.71814800	H	-2.35199800	2.72316500	1.35570100
H	-5.90911800	1.40092500	-0.53471700	H	-0.91257000	3.69164800	1.68105100
H	-4.79418000	0.69827600	-1.72510400	Cl	-0.16179500	-4.23590000	-1.04938000
H	-5.77898900	-0.35391500	-0.69416800				
C	-3.44649600	-1.85717900	0.08586400				

95$_{opt}$ (Acetonitrile)



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opt=calcfc freq=noraman b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=acetonitrile)

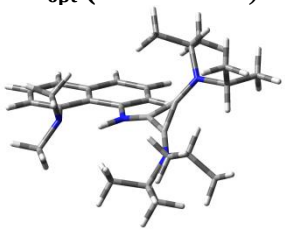
Zero-point correction=	0.149572(Hartree/Particle)
Thermal correction to Energy=	0.155088
Thermal correction to Enthalpy=	0.155889
Thermal correction to Gibbs Free Energy=	0.123748
Sum of electronic and zero-point Energies=	-343.174293
Sum of electronic and thermal Energies=	-343.168777
Sum of electronic and thermal Enthalpies=	-343.167976
Sum of electronic and thermal Free Energies=	-343.200117

0 1

N	0.67903400	-0.78532800	0.59414300	C	-0.49420400	-0.25378300	0.38829800

N	-1.66967800	2.04167900	-0.37795100	C	0.26036200	2.12904600	-1.97233500
C	-1.40261900	0.76794000	-0.00650100	H	-0.35280000	1.65220300	-2.74291500
N	-2.87816300	-1.39740600	0.35973400	H	0.85448600	1.35642600	-1.47663800
C	-1.87295800	-0.50713900	0.24470000	H	0.95256300	2.81940700	-2.46420400
C	1.75619300	-0.00203300	0.99576300	C	-2.59849000	-2.71799200	0.97261300
C	1.58594900	0.87242500	2.07823000	H	-3.56538500	-3.22702300	1.01298000
H	0.60418000	0.91174400	2.54081300	C	-1.64784700	-3.55541800	0.10679100
C	2.62268300	1.67086900	2.58576600	H	-2.04872200	-3.68841600	-0.90217800
H	2.43146400	2.32415500	3.43338300	H	-1.50550200	-4.54572100	0.55207800
C	3.86611000	1.63013500	1.99994000	H	-0.67090400	-3.06906900	0.03516300
H	4.67660400	2.25898200	2.35734000	C	-2.08131900	-2.57304200	2.41000700
C	4.10966900	0.76782000	0.89790300	H	-2.77222400	-1.98102700	3.01744000
C	5.38518600	0.82080000	0.26893200	H	-1.09957800	-2.08967800	2.42436400
H	6.12944700	1.50517800	0.66694300	H	-1.97741100	-3.56038600	2.87126600
C	5.65639600	0.04494000	-0.82825400	C	-4.23125800	-1.09354500	-0.15438400
H	6.62414900	0.09757700	-1.31968800	H	-4.14899400	-0.10603200	-0.61236300
C	4.68648200	-0.86075100	-1.30177300	C	-4.66030000	-2.06984200	-1.25935200
C	3.43437100	-0.98476600	-0.70855700	H	-3.92705900	-2.08695900	-2.07066800
C	3.07889400	-0.11654000	0.39922900	H	-5.62419800	-1.75856300	-1.67399800
C	-3.08220300	2.48134700	-0.46413500	H	-4.77964200	-3.08957800	-0.87980900
H	-3.64302500	1.75269000	0.12707300	C	-5.26638700	-1.00850300	0.97593700
C	-3.29852300	3.84791000	0.19922600	H	-4.96357600	-0.27412400	1.72811200
H	-2.94742700	3.83924100	1.23469900	H	-5.39921500	-1.97427000	1.47447400
H	-4.36612800	4.08853300	0.20034100	H	-6.23895800	-0.70863300	0.57325000
H	-2.78228500	4.65110800	-0.33560500	N	2.52646900	-1.96353700	-1.19659000
C	-3.61858800	2.45249600	-1.90403200	H	4.94663500	-1.50586400	-2.13212100
H	-3.48277200	1.46554800	-2.35676400	C	2.33691400	-3.10155600	-0.29510800
H	-3.11208800	3.18864300	-2.53679300	H	3.23558100	-3.74328000	-0.25566800
H	-4.68726800	2.68956800	-1.91372200	H	2.09422700	-2.75389200	0.70673900
C	-0.61408400	2.89953200	-0.97545300	H	1.49950200	-3.71029500	-0.64977600
H	-1.15854500	3.65940400	-1.54382400	C	2.71339600	-2.41157300	-2.57008200
C	0.22096900	3.62395200	0.08808700	H	2.83041700	-1.55280200	-3.23567600
H	-0.41701000	4.20947600	0.75571900	H	3.57987700	-3.08198500	-2.71432800
H	0.92852300	4.30739700	-0.39376000	H	1.82071900	-2.96648600	-2.87718300
H	0.78994900	2.91255600	0.69141800				

102$_{opt}$ (Acetonitrile)



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opt=calcfc freq=noraman b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=acetonitrile)

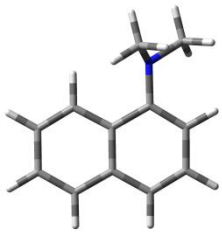
Zero-point correction= 0.638390 (Hartree/Particle)
Thermal correction to Energy= 0.672513
Thermal correction to Enthalpy= 0.673457
Thermal correction to Gibbs Free Energy= 0.572796
Sum of electronic and zero-point Energies= -1271.808994
Sum of electronic and thermal Energies= -1271.774871
Sum of electronic and thermal Enthalpies= -1271.773927
Sum of electronic and thermal Free Energies= -1271.874588

1 1

N	-0.80857000	-0.40089000	-0.31986300	H	-1.18747800	-1.27371200	0.10359100

C	0.50231200	-0.10692800	-0.22697600
N	2.08128800	1.93374900	0.35395500
C	1.57039200	0.74423400	0.04535700
N	2.59289000	-1.66007400	-0.41596600
C	1.79091000	-0.61778000	-0.24642500
C	-1.83164400	0.47621400	-0.72041400
C	-1.55337800	1.53997400	-1.56138500
H	-0.54019900	1.67410400	-1.92482000
C	-2.56861600	2.42767500	-1.97332800
H	-2.31459100	3.25715600	-2.62573000
C	-3.86465700	2.23395800	-1.56199800
H	-4.65404200	2.91144400	-1.87263200
C	-4.20246600	1.12679000	-0.73668300
C	-5.55283800	0.92079500	-0.34824100
H	-6.30205100	1.63039900	-0.68694400
C	-5.90790100	-0.15361900	0.43064300
H	-6.94188200	-0.30632500	0.72361100
C	-4.92191400	-1.07194100	0.84714800
C	-3.59393400	-0.91771900	0.49559800
C	-3.18463700	0.20564500	-0.30063300
C	3.55953300	2.12189100	0.25481100
H	3.90362900	1.31025900	-0.38984100
C	3.92103900	3.43276600	-0.45101100
H	3.44663300	3.49622000	-1.43364500
H	5.00502100	3.47167600	-0.59179200
H	3.63515400	4.31036500	0.13591800
C	4.24457300	1.99023400	1.62143300
H	3.98100400	1.04787800	2.11056400
H	3.97216900	2.81024400	2.29273100
H	5.33050500	2.01804000	1.49201000
C	1.27553200	2.98153700	1.05534600
H	2.01938700	3.55969100	1.60928700
C	0.56381000	3.93738200	0.09187800
H	1.25229000	4.35154700	-0.64771800
H	0.13596200	4.76895900	0.66069200
H	-0.25130400	3.43659200	-0.43363800
C	0.31722000	2.37309100	2.08317200
H	0.84721200	1.71505200	2.77744000
H	-0.48849600	1.80649400	1.60813200
H	-0.14515400	3.17851200	2.66046600
C	2.03468100	-2.94258900	-0.93714900
H	2.90949900	-3.56672100	-1.13108600
C	1.17151700	-3.65055800	0.11334600
H	1.73258500	-3.82835600	1.03378600
H	0.83314800	-4.61549600	-0.27527300
H	0.28253200	-3.06447500	0.36440800
C	1.30204400	-2.73841000	-2.26720200
H	1.94736600	-2.24263800	-2.99742800
H	0.39422300	-2.14089900	-2.14258400
H	1.00725800	-3.71031500	-2.67304400
C	4.04617500	-1.56721900	-0.10350400
H	4.17869900	-0.58143300	0.34378000
C	4.46654900	-2.60236900	0.94628000
H	3.86104400	-2.51153200	1.85203100
H	5.51323800	-2.43474800	1.21585200
H	4.38444500	-3.62675600	0.57094500
C	4.89699200	-1.63894900	-1.37675100
H	4.59962700	-0.86747400	-2.09264500
H	4.81440700	-2.61424500	-1.86641500
H	5.94991800	-1.48555500	-1.12299700
N	-2.61632300	-1.90943100	0.92613200
H	-5.21562600	-1.92264600	1.45329700
C	-2.97569200	-3.28812700	0.55267300
H	-3.84520700	-3.67331500	1.10381200
H	-3.19144100	-3.33086800	-0.51687800
H	-2.12508600	-3.94199400	0.76429400
C	-2.30926600	-1.79406000	2.36400500
H	-1.96677200	-0.78000300	2.58408500
H	-3.18091800	-2.01413800	2.99727700
H	-1.50972200	-2.49598500	2.61733300

110



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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

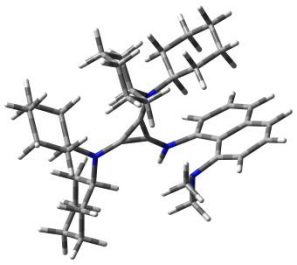
Zero-point correction= 0.220818 (Hartree/Particle)
Thermal correction to Energy= 0.231666
Thermal correction to Enthalpy= 0.232610
Thermal correction to Gibbs Free Energy= 0.184741
Sum of electronic and zero-point Energies= -519.653547
Sum of electronic and thermal Energies= -519.642699

Sum of electronic and thermal Enthalpies= -519.641755
Sum of electronic and thermal Free Energies= -519.689624

0 1

C	0.74627300	-1.54841300	-0.26719800
C	2.06445700	-1.94914300	-0.25313800
H	2.31396000	-2.99514700	-0.40647300
C	3.09765100	-1.00332000	-0.05820900
H	4.13345800	-1.32983400	-0.04180700
C	2.78989800	0.33034100	0.08551800
H	3.57968100	1.06693500	0.20918700
C	1.44208300	0.77991600	0.06369700
C	1.11781900	2.16097800	0.15205700
H	1.92136100	2.88541300	0.25200200
C	-0.19267700	2.56726200	0.09106700
H	-0.44071900	3.62354200	0.14485400
C	-1.23874400	1.62025300	-0.01147900
C	-0.97546800	0.26268600	-0.07403700
C	0.39246000	-0.18519000	-0.08164100
N	-2.00760100	-0.71559100	-0.15669500
H	-2.26416800	1.97325100	-0.01637800
C	-3.26984900	-0.27908300	-0.73564500
H	-3.86608600	0.37063800	-0.06978400
H	-3.08477000	0.25869000	-1.66853500
H	-3.87770300	-1.16174700	-0.96048200
C	-2.22079200	-1.48104400	1.07528800
H	-1.26672800	-1.81166400	1.48733700
H	-2.74206700	-0.89013400	1.84864300
H	-2.82761900	-2.36597800	0.85499900
H	-0.04406400	-2.26629000	-0.45437400

111



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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.816218 (Hartree/Particle)
Thermal correction to Energy= 0.850280
Thermal correction to Enthalpy= 0.851224
Thermal correction to Gibbs Free Energy= 0.748509
Sum of electronic and zero-point Energies= -1738.532501
Sum of electronic and thermal Energies= -1738.498439
Sum of electronic and thermal Enthalpies= -1738.497495
Sum of electronic and thermal Free Energies= -1738.600210

1 1

N	0.69253300	-2.19659800	-0.86843200
H	0.19882900	-3.03468800	-1.13848000
N	-2.58562300	-0.70051700	-0.23455500
N	0.55522700	1.40883700	-0.23564600
C	-0.03202100	-1.10866200	-0.56653800
C	-1.26582600	-0.52998700	-0.34079100
C	-0.10495800	0.25575500	-0.34506600
C	2.14006300	-2.21752300	-0.87790900
C	2.95826400	-1.99263900	0.28719000
C	2.50243800	-1.84256900	1.65375500
C	3.41567600	-1.52706500	2.64933800
H	3.07218800	-1.42458400	3.67162500
C	4.79288400	-1.37792300	2.38272800
H	5.47100100	-1.13556100	3.19481400
C	5.27191500	-1.59332700	1.11211000
H	6.33400200	-1.52887900	0.89791000
C	4.38091000	-1.90783700	0.05218800
C	4.91669500	-2.15584300	-1.24078000
H	5.99366100	-2.10868400	-1.37045300
C	4.09813200	-2.46448600	-2.30375200
H	4.51298300	-2.67065900	-3.28473800
C	2.70065600	-2.46672100	-2.11669000
H	2.04090500	-2.63058600	-2.96316900
C	0.73804700	-3.47422600	1.94973000
C	0.62371800	-1.40152200	3.17167700
H	1.13467800	-3.96884100	1.06257800
H	-0.35463400	-3.55538600	1.93877600
H	-0.46993900	-1.45629200	3.16678700
H	0.91745100	-0.34943000	3.17328200
N	1.12766300	-2.05885000	1.96976700
H	1.11258600	-4.01711100	2.83258800
H	0.96900400	-1.86245100	4.11214400

C	-3.06036800	-2.11800600	-0.25642400	C	-0.14875100	2.58021500	0.36638700
C	-4.05019100	-2.42662700	0.87910100	C	0.23303900	2.80152500	1.84504900
C	-3.62110700	-2.53319600	-1.62854600	C	-0.04509900	3.87851300	-0.45337500
H	-2.16379900	-2.72034100	-0.06483900	H	-1.20393200	2.29324600	0.35773800
C	-4.45186500	-3.91207500	0.86411500	C	-0.60060200	3.93261200	2.47051400
H	-4.95345700	-1.81425300	0.76508500	H	1.29426100	3.05373400	1.92513500
H	-3.60040300	-2.15763200	1.84141400	H	0.08563800	1.86574500	2.39692800
C	-4.02801700	-4.01702700	-1.63258800	C	-0.86397100	5.00827400	0.19709300
H	-4.49862400	-1.91942700	-1.86991500	H	0.99820400	4.20118700	-0.52516600
H	-2.87447400	-2.33420100	-2.40701300	H	-0.39503000	3.69933200	-1.47592800
C	-5.01440500	-4.33503500	-0.50017700	C	-0.47479800	5.23198100	1.66406000
H	-5.18373500	-4.09940700	1.65662400	H	-0.28351100	4.08904700	3.50706600
H	-3.57331400	-4.52785200	1.10329900	H	-1.65727700	3.63236400	2.51313700
H	-4.45945300	-4.27698800	-2.60474900	H	-0.72928100	5.92821700	-0.38155600
H	-3.12969100	-4.64027000	-1.51607000	H	-1.93333000	4.76396900	0.14071700
H	-5.25064400	-5.40425300	-0.49528100	H	-1.10116100	6.01485800	2.10470700
H	-5.96090200	-3.80823600	-0.68379000	H	0.56087600	5.59494000	1.71656600
C	-3.59424000	0.38475900	-0.34570100	C	1.94793000	1.43361900	-0.79605800
C	-3.82469900	1.14281100	0.97258700	C	1.97646300	1.91251800	-2.26230400
C	-3.34464300	1.33343800	-1.52961900	C	2.97864800	2.17454500	0.07115500
H	-4.52615900	-0.14402400	-0.56936700	H	2.25354300	0.38411900	-0.80001800
C	-4.98229700	2.14501300	0.82093700	C	3.39029800	1.78154000	-2.85236800
H	-2.90931200	1.67228700	1.26387400	H	1.65685100	2.95756200	-2.32493400
H	-4.03939800	0.42857100	1.77417300	H	1.26027400	1.32517500	-2.84958400
C	-4.50616500	2.33326000	-1.66852800	C	4.38610700	2.05850200	-0.54385500
H	-2.40571400	1.88206000	-1.38712300	H	2.72114700	3.23540400	0.15681900
H	-3.23146800	0.74763200	-2.44891300	H	2.97944900	1.75520900	1.08239600
C	-4.76393800	3.09891100	-0.36255000	C	4.42059100	2.53642700	-2.00167600
H	-5.10666900	2.70943800	1.75113000	H	3.39247100	2.15407200	-3.88242400
H	-5.91820600	1.58929700	0.67060000	H	3.66747200	0.71974900	-2.90152100
H	-4.29529900	3.03005700	-2.48660600	H	5.09087400	2.63368500	0.06627100
H	-5.41554100	1.78765000	-1.95508200	H	4.71452600	1.01281500	-0.49583800
H	-5.63061200	3.75806600	-0.47912300	H	5.42546400	2.40413300	-2.41714000
H	-3.90635200	3.75097900	-0.14875600	H	4.20729700	3.61379900	-2.04105300

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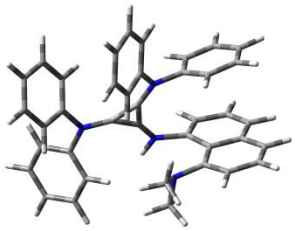

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.532875 (Hartree/Particle)
Thermal correction to Energy= 0.562095
Thermal correction to Enthalpy= 0.563039
Thermal correction to Gibbs Free Energy= 0.466384
Sum of electronic and zero-point Energies= -1724.278565
Sum of electronic and thermal Energies= -1724.249345
Sum of electronic and thermal Enthalpies= -1724.248401
Sum of electronic and thermal Free Energies= -1724.345056

1 1

N	0.90243900	-1.86413300	-0.94485100	H	0.53354000	-2.79909700	-1.05795600

N	-2.57164700	-0.89401400	-0.33169300
N	0.20680700	1.67374100	-0.29784300
C	0.01680700	-0.90227100	-0.64428600
C	-1.29309600	-0.52173800	-0.42628700
C	-0.26708500	0.43338000	-0.41761800
C	2.33597600	-1.66173400	-0.94241300
C	3.10101300	-1.32000300	0.23034000
C	2.61726800	-1.24941800	1.59372000
C	3.46352100	-0.80253400	2.59815200
H	3.10248700	-0.76232300	3.61901300
C	4.80329300	-0.44166900	2.34357200
H	5.42973500	-0.10176600	3.16228400
C	5.31931200	-0.57378000	1.07605100
H	6.36066000	-0.34624000	0.87121000
C	4.49535700	-1.01590400	0.00746900
C	5.07263900	-1.17136800	-1.28207100
H	6.13013100	-0.95659900	-1.40255800
C	4.31937900	-1.59652400	-2.35307800
H	4.76799200	-1.73111600	-3.33164200
C	2.93755000	-1.81490700	-2.17758800
H	2.31656300	-2.07939000	-3.02784000
C	1.31042600	-3.21029300	2.01815000
C	0.67201000	-1.14371600	3.08764400
H	1.70888400	-3.65700800	1.10458200
H	0.28934600	-3.57316600	2.17039200
H	-0.38282000	-1.43761600	3.10466200
H	0.72877300	-0.05411400	3.02585700
N	1.30741700	-1.74250500	1.91374600
H	1.92438800	-3.56347100	2.86221500
H	1.11103600	-1.45945100	4.04826000
C	-2.90005100	-2.29532900	-0.41824400
C	-2.12829200	-3.23465700	0.27166900
C	-3.97902600	-2.70721200	-1.20669400
C	-2.42640000	-4.59332400	0.15501800
H	-1.31974600	-2.89975600	0.91154200
C	-4.27577100	-4.06563100	-1.30333100
H	-4.57458400	-1.97377100	-1.73874500
C	-3.50012800	-5.01267000	-0.63061000
H	-1.82924900	-5.32100900	0.69594600
H	-5.11277100	-4.38427000	-1.91630300
H	-3.73629900	-6.06839100	-0.71288800
C	-3.62139900	0.09734800	-0.27285000
C	-3.66062000	1.13500300	-1.20644800
C	-4.59852200	-0.00725700	0.72083800
C	-4.67638800	2.08835100	-1.12907700
H	-2.90956100	1.19303900	-1.98793400
C	-5.61786400	0.94122200	0.77904500
H	-4.55883000	-0.82328300	1.43483300
C	-5.65636000	1.99203100	-0.14063000
H	-4.70690500	2.89731600	-1.85166200
H	-6.37943500	0.86164800	1.54819500
H	-6.45090300	2.72939700	-0.08986200
C	-0.62720400	2.71442100	0.25811800
C	-0.67469900	3.96550000	-0.36380500
C	-1.36786300	2.46925100	1.41734600
C	-1.47570000	4.96893600	0.17824400
H	-0.08922500	4.14869600	-1.25819200
C	-2.17797100	3.47611600	1.94203500
H	-1.30647800	1.50348500	1.90909700
C	-2.23209200	4.72734300	1.32717800
H	-1.51174200	5.94080600	-0.30362100
H	-2.75459800	3.28391500	2.84109600
H	-2.85459200	5.51234800	1.74401200
C	1.54011400	2.00288100	-0.74774600
C	1.91448800	1.74799700	-2.06811800
C	2.42288900	2.62379100	0.13984100
C	3.19255100	2.10674100	-2.49850900
H	1.20942300	1.28877000	-2.75387900
C	3.69261700	2.98797100	-0.30320200
H	2.11246200	2.82186200	1.16011700
C	4.07969900	2.72969200	-1.62038500
H	3.48618300	1.91254500	-3.52496500
H	4.38042000	3.47153000	0.38284100
H	5.06835500	3.01862100	-1.96225500

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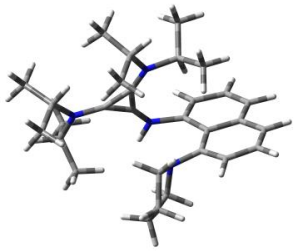

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.531446 (Hartree/Particle)
Thermal correction to Energy= 0.545899
Thermal correction to Enthalpy= 0.546843
Thermal correction to Gibbs Free Energy= 0.487640
Sum of electronic and zero-point Energies= -1349.272569
Sum of electronic and thermal Energies= -1349.258116

Sum of electronic and thermal Enthalpies= -1349.257172
Sum of electronic and thermal Free Energies= -1349.316375

1 1

N	-0.43548000	-0.55131900	1.76062400	C	2.99664200	-1.32629100	2.96893700
H	-0.18319300	-1.42424300	2.20318300	H	3.25298600	-2.19324500	3.58425100
N	3.04354000	-0.42927800	0.63461600	H	3.58393300	-0.47325500	3.31865100
N	0.52405900	2.14201600	-0.52942000	H	1.93995600	-1.09840900	3.13984400
C	0.50466900	0.03492200	1.00411700	C	-0.81549500	2.73987700	-0.25991600
C	1.81900100	0.10004000	0.58403900	H	-1.30387000	2.06383300	0.44299000
C	0.88961200	1.05739200	0.15423100	C	-0.68331700	4.12420000	0.40710700
C	-1.83828600	-0.19667500	1.71202500	H	-1.67801700	4.49856500	0.66529200
C	-2.67166600	-0.35726600	0.54707800	H	-0.09266600	4.06991200	1.32603900
C	-2.30935600	-1.00062800	-0.69896100	H	-0.22284500	4.85722700	-0.26191100
C	-3.19820100	-0.97977400	-1.76397500	C	-1.67131900	2.81453000	-1.53533800
H	-2.93352600	-1.48825500	-2.68449700	H	-2.67309800	3.16924800	-1.27804300
C	-4.46996400	-0.37713200	-1.66667600	H	-1.25769000	3.51267400	-2.26937300
H	-5.13639100	-0.39324500	-2.52338500	H	-1.77205900	1.83110200	-2.00092900
C	-4.87869800	0.17128300	-0.47398400	C	1.45235700	2.85407500	-1.44742700
H	-5.87275000	0.59360300	-0.36624300	H	0.85004700	3.65411200	-1.88121900
C	-4.00569100	0.18769300	0.64576200	C	2.61832200	3.52265800	-0.69313800
C	-4.47533800	0.73380500	1.87113100	H	3.27873900	4.03281600	-1.40036800
H	-5.49302300	1.11022600	1.91174100	H	2.24523300	4.26499700	0.01654600
C	-3.67063000	0.77500200	2.98735800	H	3.21924500	2.80413300	-0.13178300
H	-4.03879400	1.17819500	3.92474000	C	1.89876000	1.94994500	-2.60828200
C	-2.33674600	0.32877500	2.88950000	H	2.54528300	2.50947600	-3.29003800
H	-1.66667100	0.42244600	3.73807300	H	2.45474300	1.07397400	-2.26597800
C	4.16334600	0.12879700	-0.16238100	H	1.03222200	1.59572500	-3.17306600
H	3.74865200	0.99323000	-0.67789900	C	-1.24192300	-3.13846300	-0.22397200
C	4.64730900	-0.86733800	-1.23332100	C	-0.41106500	-1.85652400	-2.08781600
H	5.41653400	-0.39709300	-1.85249800	C	-0.46881000	-4.06014800	-1.18485300
H	5.08995100	-1.76311700	-0.78721800	H	-2.30179800	-3.41950500	-0.18946300
H	3.82526900	-1.17740200	-1.88509000	H	-0.85946000	-3.20199300	0.80292400
C	5.30971500	0.62650800	0.73815700	C	-0.54185500	-3.31904900	-2.52778100
H	6.07358200	1.11170500	0.12382900	H	0.65109300	-1.60425100	-1.95035300
H	4.94787400	1.35270600	1.47159400	H	-0.81706700	-1.13773700	-2.80230300
H	5.79704200	-0.19234900	1.27532500	H	0.57496600	-4.15935300	-0.86866800
C	3.28805600	-1.62870400	1.48532400	H	-0.89897400	-5.06414000	-1.21755900
H	4.35435600	-1.83830100	1.38616900	H	0.23579100	-3.62502300	-3.23294500
C	2.50710700	-2.85476000	0.98456800	H	-1.51346800	-3.49118900	-3.00481400
H	2.74029400	-3.72625900	1.60293400	N	-1.10002900	-1.75762000	-0.77846800
H	1.42753500	-2.68770100	1.03177500				
H	2.76619500	-3.09092600	-0.05080200				

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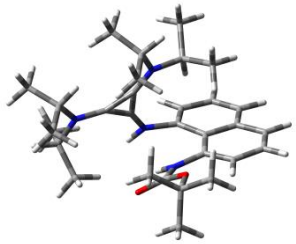

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.565873 (Hartree/Particle)

Thermal correction to Energy= 0.585164
Thermal correction to Enthalpy= 0.586109
Thermal correction to Gibbs Free Energy= 0.515171
Sum of electronic and zero-point Energies= -1539.049965
Sum of electronic and thermal Energies= -1539.030673
Sum of electronic and thermal Enthalpies= -1539.029729
Sum of electronic and thermal Free Energies= -1539.100667

1 1

N	-0.49148400	-1.68173900	-1.68470200	H	3.50747300	-3.21765600	-2.28490700
H	-0.15132400	-1.92930600	-2.60403300	H	1.90249000	-2.65209900	-2.76052800
N	2.98317800	-0.96950700	-0.78702800	C	-1.07339900	-1.77498700	2.15087400
N	0.30675200	-1.28521500	1.86841700	H	-1.52223300	-1.97063500	1.17615100
C	0.41462600	-1.41383400	-0.73230900	C	-1.04344700	-3.09579700	2.94667900
C	1.72595400	-1.15960100	-0.38023100	H	-2.06402700	-3.47119500	3.06320800
C	0.73807100	-1.28055200	0.60692700	H	-0.45737100	-3.86094700	2.42959600
C	-1.91463100	-1.76964400	-1.43385600	H	-0.63018600	-2.95833300	3.95022500
C	-2.72228500	-0.66917000	-0.97118400	C	-1.91831100	-0.70977400	2.86931300
C	-2.30323600	0.70734900	-0.80569000	H	-2.94464800	-1.07270800	2.97160700
C	-3.17971600	1.62764400	-0.24929600	H	-1.54590200	-0.49957100	3.87652500
H	-2.85540200	2.65121200	-0.13997500	H	-1.94500200	0.22364600	2.30151600
C	-4.49068000	1.27604200	0.13511900	C	1.19420900	-0.95056900	3.01381400
H	-5.13946100	2.03432900	0.56072500	H	0.54251800	-0.99694500	3.88788600
C	-4.94897000	-0.00179300	-0.08269900	C	2.30342900	-2.00110300	3.21738100
H	-5.96907100	-0.27957000	0.16237100	H	2.93414500	-1.71861100	4.06518000
C	-4.09143500	-0.98748000	-0.63884500	H	1.87319400	-2.98315200	3.42820000
C	-4.61069200	-2.28852900	-0.87963200	H	2.94639600	-2.10363000	2.34106700
H	-5.65185900	-2.47948300	-0.63904500	C	1.71403900	0.49343600	2.91927600
C	-3.82294800	-3.28164500	-1.41665700	H	2.31790400	0.73061500	3.79959200
H	-4.22736200	-4.26870400	-1.61352000	H	2.33356200	0.65866800	2.03484400
C	-2.46069500	-3.01801500	-1.66707400	H	0.87729200	1.19573700	2.87615600
H	-1.81069500	-3.81500000	-2.01518400	N	-1.03071200	1.10517000	-1.27035800
C	4.07088300	-0.66073100	0.17327100	C	-0.23154100	2.21115900	-1.01756700
H	3.60300600	-0.68231500	1.15593500	C	-0.03519900	4.28620200	0.29625300
C	4.63348600	0.75667900	-0.04545900	C	1.39878100	4.05367200	0.77582000
H	5.36274600	0.98573600	0.73686800	H	1.41263600	3.35607200	1.61884100
H	5.14588500	0.84721300	-1.00784100	H	2.02263000	3.66187300	-0.02742100
H	3.83816200	1.50630100	-0.00985100	H	1.82223800	5.00252100	1.11866200
C	5.17063000	-1.73915200	0.15300100	C	-0.10121300	5.20163800	-0.92749900
H	5.90285400	-1.52844000	0.93764400	H	0.50085300	4.81177000	-1.74867900
H	4.75260400	-2.73380600	0.33328000	H	-1.13523900	5.31820000	-1.26554100
H	5.71143000	-1.75920900	-0.79766200	H	0.27776000	6.19186000	-0.65755600
C	3.29976700	-1.03605700	-2.24217700	C	-0.91119500	4.81782500	1.43096800
H	4.37917500	-0.88877500	-2.30349800	H	-0.52453800	5.78013200	1.77716800
C	2.60996400	0.08947200	-3.03034400	H	-1.94127300	4.96632800	1.09504200
H	2.99565800	0.10942000	-4.05406800	H	-0.91771800	4.12477800	2.27699200
H	1.52915100	-0.06940800	-3.09164900	O	-0.68427800	2.98132400	-0.02176100
H	2.76520800	1.06703000	-2.57377500	O	0.79313700	2.38288000	-1.66061400
C	2.97214400	-2.42800700	-2.81890900	H	-0.64659900	0.56437600	-2.02846900
H	3.25957300	-2.47097000	-3.87300100				

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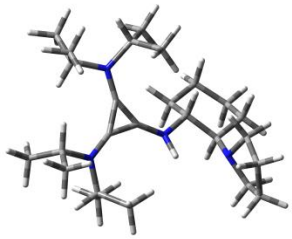

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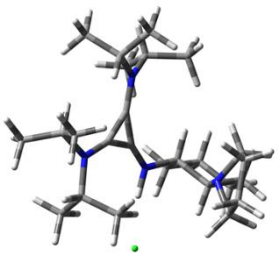
opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.698867 (Hartree/Particle)
Thermal correction to Energy= 0.732080
Thermal correction to Enthalpy= 0.733024
Thermal correction to Gibbs Free Energy= 0.634128
Sum of electronic and zero-point Energies= -1199.107395
Sum of electronic and thermal Energies= -1199.074182
Sum of electronic and thermal Enthalpies= -1199.073238
Sum of electronic and thermal Free Energies= -1199.172134

1 1

C	-4.27685100	-2.15816400	-1.82671600	C	3.63092600	-1.84924900	0.27949800
C	-2.87485100	-2.78242800	-1.89867300	H	3.88803600	-0.99773400	-0.35643800
C	-1.77462300	-1.71211300	-1.82119300	C	3.73554600	1.90874200	-0.07452000
C	-1.94384600	-0.85484100	-0.55661600	H	3.95009300	0.96462500	0.43169000
C	-3.33003100	-0.16243600	-0.58873400	C	1.62121400	3.01166600	-1.05525400
C	-4.43275300	-1.24140900	-0.60126400	H	2.42700500	3.72774400	-1.23358300
H	-0.78258300	-2.17581000	-1.84273300	C	4.04658200	-3.11621400	-0.47766500
H	-2.74985200	-3.49416300	-1.07065800	H	3.53505700	-3.18622700	-1.44122200
H	-2.76280000	-3.36052000	-2.82167600	H	5.12390500	-3.09079200	-0.66490800
H	-4.45915800	-1.57331000	-2.73829200	H	3.83861900	-4.02554600	0.09385000
H	-5.03888300	-2.94406300	-1.80560800	C	4.36825000	-1.69956600	1.61681900
H	-1.89125800	-1.50261900	0.33129000	H	4.17100600	-2.54121800	2.28779900
H	-3.38173500	0.36980800	-1.55015400	H	5.44835600	-1.66852500	1.44574800
H	-4.38057000	-1.84108200	0.31638500	H	4.07704200	-0.77990700	2.13355800
H	-5.41870800	-0.76529900	-0.61146800	C	0.66087700	-2.31519300	2.38138600
H	-1.82735800	-1.04992200	-2.69492200	H	0.24020000	-3.14403800	2.95750800
N	-0.94063500	0.21171100	-0.45428000	H	1.29766500	-1.72649400	3.04742700
H	-1.37396700	1.10493800	-0.21035600	H	-0.17264600	-1.68395400	2.05738400
C	0.36968200	0.06895500	-0.24494500	C	0.61485900	-3.76821000	0.28694600
C	1.51938700	-0.64937500	0.08678700	H	0.27707100	-4.64193800	0.85243100
C	1.60462000	0.70913400	-0.24688100	H	-0.27337600	-3.25162600	-0.08191000
C	-4.45117800	1.90359500	0.22630000	H	1.19040900	-4.12138600	-0.57206100
C	-3.53580200	0.48312400	1.83882700	C	4.00064500	3.03601000	0.93079200
C	-4.40046000	2.74989600	1.51416100	H	3.37196700	2.93129200	1.81928400
H	-5.44739300	1.44442200	0.11360400	H	5.04670300	3.00130900	1.24836100
H	-4.24997900	2.48002500	-0.68249100	H	3.82715600	4.02511700	0.49678400
C	-3.73700600	1.82138800	2.57175800	C	4.62950800	2.00678400	-1.31655600
H	-2.64631100	-0.05936400	2.17697200	H	5.68224800	1.98654200	-1.02023600
H	-4.40656600	-0.17402200	1.99677200	H	4.44973800	1.17341300	-2.00209900
H	-3.80275200	3.65264000	1.36373300	H	4.46358100	2.93976700	-1.86415900
H	-5.40083800	3.07125900	1.81297300	C	0.99279700	2.66809900	-2.41046800
H	-2.77326300	2.22983600	2.88874000	H	0.15656700	1.97028800	-2.30494800
H	-4.34863800	1.69823500	3.46853700	H	0.60799400	3.57825300	-2.87931500
N	-3.40311800	0.88890300	0.43022500	H	1.72986800	2.22414300	-3.08514300
N	2.15023300	-1.77319700	0.44342000	C	0.62402400	3.65804800	-0.08547600
N	2.29531100	1.82782300	-0.44632000	H	1.10579300	3.93973700	0.85404700
C	1.45637000	-2.86263300	1.19138800	H	0.19825100	4.56012900	-0.53421100
H	2.27177300	-3.46762500	1.59466800	H	-0.20732000	2.98531600	0.14955100

115 – Cl^-



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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.698609 (Hartree/Particle)
Thermal correction to Energy= 0.734721
Thermal correction to Enthalpy= 0.735665
Thermal correction to Gibbs Free Energy= 0.628877
Sum of electronic and zero-point Energies= -1659.496654
Sum of electronic and thermal Energies= -1659.460542
Sum of electronic and thermal Enthalpies= -1659.459597
Sum of electronic and thermal Free Energies= -1659.566385

1 1

C	5.02050400	0.86092400	-1.19338700	N	-1.79743300	2.08075900	-0.12818500
C	4.05301900	1.39337100	-2.25797600	N	-2.45774700	-1.56602500	-0.19636500
C	2.75840300	0.57152300	-2.29001600	C	-1.11595600	3.25607100	-0.72779700
C	2.07280900	0.50512600	-0.91178900	H	-1.88451900	4.03477700	-0.76020300
C	3.05665200	-0.02559900	0.16837900	C	-3.12405400	2.27195000	0.50313300
C	4.34552300	0.82357100	0.18479100	H	-3.36406800	1.30812500	0.95884900
H	2.05573900	0.98282700	-3.02526600	C	-3.90641100	-1.30042600	-0.04337900
H	3.81891400	2.44644100	-2.04058700	H	-4.02444800	-0.22924600	-0.21936700
H	4.52386700	1.37864300	-3.24775800	C	-1.97104700	-2.97997100	-0.16234600
H	5.34017400	-0.15219800	-1.46959900	H	-2.85215400	-3.55112500	0.14578300
H	5.92541200	1.47955200	-1.15545700	C	-4.21633800	2.60681600	-0.52485500
H	1.72458600	1.50378500	-0.62499800	H	-4.26005600	1.85343400	-1.31708200
H	3.31586600	-1.03929600	-0.16043100	H	-5.19609000	2.65013100	-0.03828900
H	4.11383400	1.85247300	0.49579800	H	-4.04273500	3.57998000	-0.99546000
H	5.03447500	0.41918000	0.93591900	C	-3.07884600	3.29815800	1.64359900
H	2.97166500	-0.45905100	-2.59995500	H	-2.86388900	4.30835000	1.28153900
N	0.90581200	-0.38080800	-0.99626600	H	-4.05134500	3.33261400	2.14450300
H	1.16683800	-1.39921400	-1.14775200	H	-2.32190900	3.02667100	2.38405700
C	-0.31336300	-0.08146800	-0.61744500	C	0.02865100	3.78356800	0.14796000
C	-1.34317200	0.81935800	-0.31708100	H	0.46324400	4.68326300	-0.29994700
C	-1.60918100	-0.54169400	-0.34047900	H	-0.32622400	4.03891500	1.14936800
C	2.85626200	-1.31659800	2.27283800	H	0.82564600	3.04445600	0.25368800
C	2.31649400	0.94222600	2.38800900	C	-0.68420000	2.99615000	-2.17602300
C	2.05789100	-1.17364000	3.58499300	H	-0.28178300	3.91519500	-2.61240300
H	3.94132500	-1.25669000	2.48700900	H	0.09273100	2.23099100	-2.24248200
H	2.67411700	-2.25478700	1.74139000	H	-1.53356800	2.67227000	-2.78443000
C	1.63964800	0.32511900	3.62689600	C	-4.39379100	-1.60751700	1.38018200
H	1.74291800	1.77402900	1.96310200	H	-4.29916900	-2.67186500	1.61612900
H	3.31061000	1.34016800	2.66792500	H	-3.81869700	-1.04617200	2.12278500
H	1.17494300	-1.81868100	3.57274300	H	-5.44979900	-1.33865600	1.48611100
H	2.65906000	-1.46095200	4.45236300	C	-4.74443700	-2.01905400	-1.11046500
H	0.55215500	0.41924700	3.54938400	H	-5.79402000	-1.72422500	-1.01190100
H	1.94768300	0.82738100	4.54884500	H	-4.40684400	-1.75590100	-2.11642600
N	2.39232300	-0.18557900	1.46381200	H	-4.69773000	-3.10679900	-1.00721300

C	-1.53955700	-3.47605000	-1.54698500	H	-1.22935200	-2.80677500	1.87796200
H	-0.59962400	-3.01980500	-1.86813900	H	-0.67425100	-4.24915700	1.00195500
H	-1.35207200	-4.55322700	-1.50489100	H	0.05008100	-2.70153800	0.63008400
H	-2.31943600	-3.29112100	-2.29184300	Cl	2.07491400	-3.13863400	-1.37921400
C	-0.89155900	-3.18159100	0.90595000				

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.550678 (Hartree/Particle)
Thermal correction to Energy= 0.579356
Thermal correction to Enthalpy= 0.580300
Thermal correction to Gibbs Free Energy= 0.492693
Sum of electronic and zero-point Energies= -910.430086
Sum of electronic and thermal Energies= -910.401408
Sum of electronic and thermal Enthalpies= -910.400464
Sum of electronic and thermal Free Energies= -910.488071

1 1

N	-0.83915800	-2.18884700	0.09587200	H	-1.27274500	4.40182900	0.57006200
C	-0.28063100	-0.97573100	0.06449100	H	0.02148300	3.65663100	1.52923300
C	0.92301600	-0.27678000	0.05880600	C	-0.54109400	3.21368200	-1.90405700
C	-0.29075700	0.41781400	0.02653700	H	0.20360400	3.93702100	-2.25041900
N	2.25383200	-0.32875100	0.06730700	H	-0.51898900	2.35553200	-2.58169400
N	-0.95727600	1.57796700	-0.02823200	H	-1.51971400	3.68995600	-1.98070400
C	-2.26666000	-2.58288000	-0.11303800	C	3.98417200	0.79536300	1.48624900
C	2.93951400	-1.64214100	-0.10031600	H	4.76813700	0.04446000	1.34954200
H	4.00158600	-1.39482900	-0.16545400	H	4.48242400	1.75472100	1.65202200
C	3.06529300	0.90639900	0.26356600	H	3.41735400	0.54750300	2.38772100
H	2.33637900	1.69133400	0.48025500	C	3.82535300	1.28502800	-1.01255100
C	-2.37739600	1.57528000	0.44055900	H	3.14449100	1.40142000	-1.86077000
H	-2.68725000	0.53413600	0.32764600	H	4.35406100	2.23116400	-0.86495300
C	-0.19998300	2.79112100	-0.46608800	H	4.57424600	0.53158600	-1.27593800
H	0.83921000	2.45527200	-0.48591000	C	-2.49432700	1.92035700	1.93337600
C	-2.24478400	-4.10352000	-0.33690000	H	-2.28554700	2.97340200	2.13115300
H	-1.82451300	-4.62653600	0.52938100	H	-3.51317000	1.71500100	2.27648700
H	-3.26239600	-4.47344500	-0.48129900	H	-1.80822000	1.31496700	2.53319600
H	-1.66126000	-4.36566100	-1.22503400	C	-3.32482400	2.40850200	-0.42600000
C	-2.82134300	-1.88555500	-1.36432200	H	-3.13796700	3.48157200	-0.34249900
H	-2.80558900	-0.79618500	-1.27512000	H	-3.26829900	2.12276400	-1.47902800
H	-2.24287000	-2.16237700	-2.25025100	H	-4.34917100	2.23388900	-0.08459100
H	-3.85983200	-2.18644900	-1.52646700	C	2.54383000	-2.32057700	-1.41702400
C	-3.09096500	-2.25698600	1.14402600	H	1.48661200	-2.60454000	-1.43242300
H	-4.13138000	-2.56426700	1.00460900	H	2.72871300	-1.66150500	-2.26938400
H	-2.69308100	-2.78577900	2.01488500	H	3.13249800	-3.23151900	-1.55672100
H	-3.08626400	-1.18760900	1.37040800	C	2.74667700	-2.54637300	1.12387600
C	-0.27475800	3.95995500	0.52169400	H	3.29860200	-3.48117000	0.99138000
H	0.40924700	4.74664700	0.19001900	H	3.10735900	-2.06393100	2.03536600

H	1.69361200	-2.80319700	1.28273600	H	-0.19514200	-2.95214200	0.25062100

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.519209 (Hartree/Particle)
Thermal correction to Energy= 0.546855
Thermal correction to Enthalpy= 0.547799
Thermal correction to Gibbs Free Energy= 0.461434
Sum of electronic and zero-point Energies= -984.253188
Sum of electronic and thermal Energies= -984.225543
Sum of electronic and thermal Enthalpies= -984.224599
Sum of electronic and thermal Free Energies= -984.310963

1 1

N	1.14672800	-1.74715600	0.18559700	H	-4.98008600	-1.37977000	1.09247500
C	0.18118900	-0.82207900	0.06451500	C	2.17998600	2.77130300	-0.95054600
C	-1.17734400	-0.56163300	-0.02463500	H	1.89610400	3.80276900	-1.16397900
C	-0.25073100	0.49500200	0.00338100	H	3.25643700	2.75973200	-0.75524600
N	-2.41469400	-1.04811500	-0.07044800	H	1.99454700	2.17005300	-1.84459400
N	0.03304000	1.79728800	-0.01994800	C	1.58461300	3.09014500	1.50768900
C	-2.61624700	-2.52507600	-0.13122600	H	1.17412000	4.09010800	1.34751600
H	-3.69545100	-2.65230700	-0.24119500	H	1.09843100	2.64593300	2.38007400
C	-3.59668400	-0.14107800	-0.07600400	H	2.64675100	3.21062000	1.74012000
H	-3.18249900	0.86334000	0.02970800	C	-2.19788300	-3.20594200	1.17777000
C	1.45110900	2.19443100	0.27101300	H	-1.12541000	-3.09611400	1.37337200
H	1.93959200	1.24696500	0.51068300	H	-2.73394800	-2.78635800	2.03258500
C	-1.11829300	2.74562000	-0.15462600	H	-2.41535300	-4.27658700	1.12991600
H	-1.85327800	2.18351500	-0.73955300	C	-1.94973500	-3.13858000	-1.36805100
C	-0.79473800	3.99840100	-0.97222500	H	-2.19411000	-4.20255600	-1.43149600
H	-1.72469800	4.55073900	-1.13421000	H	-2.29751100	-2.65439100	-2.28427400
H	-0.10718400	4.67112900	-0.45503800	H	-0.85880100	-3.05270500	-1.33400900
H	-0.37862900	3.74864100	-1.95042100	H	0.84509400	-2.69144500	0.38380100
C	-1.75209700	3.08963500	1.20188800	C	2.55363500	-1.52670500	0.05385900
H	-2.69275700	3.62583200	1.04234900	C	3.05845300	-0.76466200	-1.00381300
H	-1.97052500	2.18800900	1.78252700	C	3.41992000	-2.12870700	0.97108600
H	-1.10451200	3.73004300	1.80393900	C	4.43691400	-0.58280700	-1.12278800
C	-4.34954900	-0.21161300	-1.40999700	H	2.38145900	-0.34512900	-1.74110200
H	-4.79909900	-1.19592000	-1.57299100	C	4.79649900	-1.95964600	0.82923200
H	-5.16196700	0.52068300	-1.41555300	H	3.01850400	-2.71703600	1.79106400
H	-3.68662500	0.00695400	-2.25203400	C	5.30791600	-1.18069100	-0.21069200
C	-4.50891600	-0.39299500	1.13065300	H	4.82915400	0.00604700	-1.94586200
H	-3.95689100	-0.30853900	2.07083500	H	5.46853900	-2.43065300	1.53924900
H	-5.31274900	0.34855900	1.14079600	H	6.37971100	-1.04822000	-0.31476000

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